Spectroscopic and electrochemical study of dinuclear and mononuclear copper complexes with the bidentate ligand of the 2,2´-biquinoline series

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The newly synthesized complex (**2**) of copper(I) chloride with di-*n*-hexyl 2,2´-biquinoline-4,4´-dicarboxylate (L) was spectroscopically and electrochemically characterized. The X-ray diffraction study showed that the crystals of complex **2** consist of the dinuclear moieties $[L_2Cu^I_2(\mu\text{-}Cl)_2]$ containing $Cu_2(\mu\text{-}Cl)_2$ clusters. Spectrophotometric studies and ESI-mass spectrometric measurements showed that after the dissolution of complex **2** in acetonitrile (AN) and *N*-methyl-2-pyrrolidone (NMP), the solution contained not only the dinuclear complexes $[L_2Cu^I_2(\mu\text{-}Cl)_2]$ but also $[L_2Cu^I]Cl$, $[LCu^ICl(Sol)]$, and $[Cu^ICl(Sol)]$ (Sol is the solvent). The electrochemical data also confirm the conclusion that bridged dinuclear chloride complex **2** dissociates both in NMP and AN to form the tetrahedral bis-biquinoline complex $[L_2Cu^I]Cl$. In solutions of complex **2** in alcohols and *N,N*-dimethylformamide (DMF), only $[L_2Cu^I]Cl$ and $[Cu^ICl(Sol)]$ are present. In EtOH, AN, and DMF, $[Cu^ICl(Sol)]$ undergoes disproportionation to $[Cu^{II}Cl(Sol)]$ and Cu^0.

Key words: crystal engineering, supramolecular chemistry, coordination compounds, 2,2´-biquinolines, X-ray diffraction study, mass spectrometry, electrochemistry, spectrophotometry.

Copper coordination compounds with 1,4-diimine-type ligands have attracted interest because they can be used to study the relationship between the redox, magnetic, and spectroscopic properties of the complexes, on the one hand, and the coordination geometry of the metal atom, on the other hand.[1] The ability to control the above-mentioned properties by varying the coordination environment of the metal atoms and to control the coordination of the complexes by changing the external conditions allows one to design aesthetically attractive and functionally promising structures.[2,3] In particular, the reversible Cu^I/Cu^{II} redox transition can be used to influence the macroscopic solution⇆gel transitions. The ability to control the solid-state structures of the complexes is a key concept of the so-called crystal engineering, whose main aim is to synthesize desired crystal structures from appropriately chosen molecular components.[5,6] The use of bridging ligands as linkages between individual molecules of solid-state complexes is an equally important problem. This mainly refers to simple acido ligands, such as halides and carboxylates. Due to the lability of the copper—acido

ligand bonds, it is possible to design systems, in which reversible transitions between two or several states can occur as a result of the replacement of anions by various coordinating molecules, primarily, by solvents.

2,2´-Biquinoline (biq) is the well known 1,4-diimine-type ligand. In the studies[7—9] on the monovalent copper complexes of biquinolines with different chemical structures, it was noted that these systems hold promise as catalysts for the polymerization, photocatalytic devices, and biologically active compounds.

In terms of crystal engineering, copper(II) complexes with 2,2´-bipyridine (bipy), phenanthroline (phen), and their derivatives related to 2,2´-biquinoline were studied in most detail.[10,11] In these systems, the chlorine-bridged dinuclear complexes $[L_2Cu^{II}_2(\mu\text{-}Cl)_2]\}^{2+}$ (L = bipy[10,12—18] or phen[11,19—24]) containing the metal atom in a square-pyramidal coordination environment belong to the most widespread structural type.

Copper complexes with ligands of the 2,2´-biquinoline series have not been studied in terms of crystal engineering. We found the only characterized crystal structure of

the mononuclear complex of 2,2´-biquinoline with $CuCl_2$, in which the metal atom is in a distorted tetrahedral coordination.[25] Based on numerous published data on the halogen-bridged structures, it can be expected that biquinoline complexes with CuCl can form dinuclear acido clusters $[L_2Cu^I_2(\mu\text{-}Cl)_2]$ in crystals and, probably, in solution.

The presence of carboxy groups in a heterocyclic ligand has a high potential for its further functionalization. Among these transformations, the esterification is of particular interest. Actually, a change in the lengths of the alkyl groups in alcohols used for the esterification makes it possible to control intermolecular interactions in solids. The stacking interaction between the π systems of the quinoline rings is another factor determining the mutual arrangement of the molecules in solid-state structures. In turn, the interactions of complexes with solvent molecules can break interactions characteristic of crystals and, as a consequence, can lead to substantial changes in the coordination sphere of the metal atoms and the properties of the metal complexes.

Several electrochemical studies[26,27] of copper-containing complexes with biquinolines and bipyridines were published. These studies were focused primarily on the relationship between the electrochemical oxidation potentials of the complexes and their structures in solution, which strongly depend on the nature of the solvent.[28] The electrochemical data[27] provide evidence on the possible structures of the complexes in solution, in particular, on the presence of chloride-bridged dinuclear structures.

It should be noted that the structures and stability of copper complexes with biquinoline ligands in the solid state have not been compared with those in solution. The main aims of the present study were to determine the crystal structure of the complex of copper(I) chloride with the bidentate ligand dihexyl 2,2´-biquinoline-4,4´-dicarboxylate and to investigate the possible equilibria involving copper-containing particles in different solvents by spectroscopic and electrochemical methods.

Results and Discussion

Di-*n*-hexyl 2,2´-biquinoline-4,4´-dicarboxylate (**1**, hereinafter denoted L) was synthesized in 55% yield (Scheme 1).

Crystals of the ligand suitable for X-ray diffraction were isolated from a solution of the complex $[L_2Cu^I_2(\mu\text{-}Cl)_2]$ (**2**) in DMF (Table 1). In the crystal structure, centrosymmetric molecules **1** adopt a planar *anti* conformation (with respect to the C(1)—C(1A) bond) due apparently to the fact that there is a repulsion of the hydrogen atoms in the possible *syn* conformation (Fig. 1). The ester group lies in the plane of the aromatic ring; the C(2)—C(3)—C(11)—O(1) torsion angle is 10.1°. A slight twist of the group is apparently attributed to the rather strong intramolecular C—H...O interaction (H...O, 2.12 Å) with the hydrogen
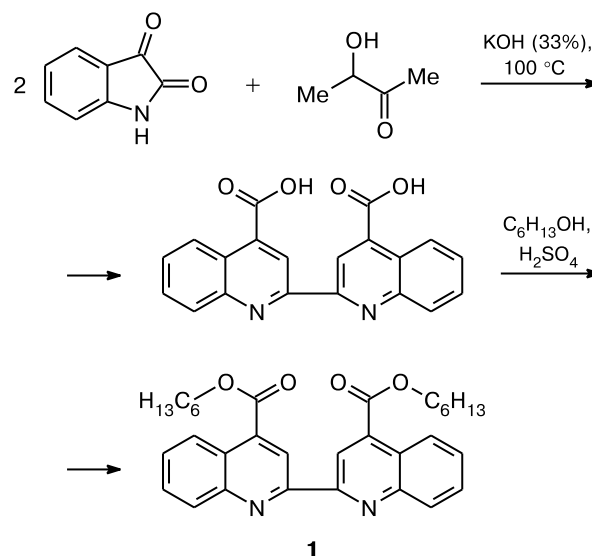
Scheme 1

1

Table 1. Principal crystallographic parameters and the structure refinement statistics for compounds **1** and **2**

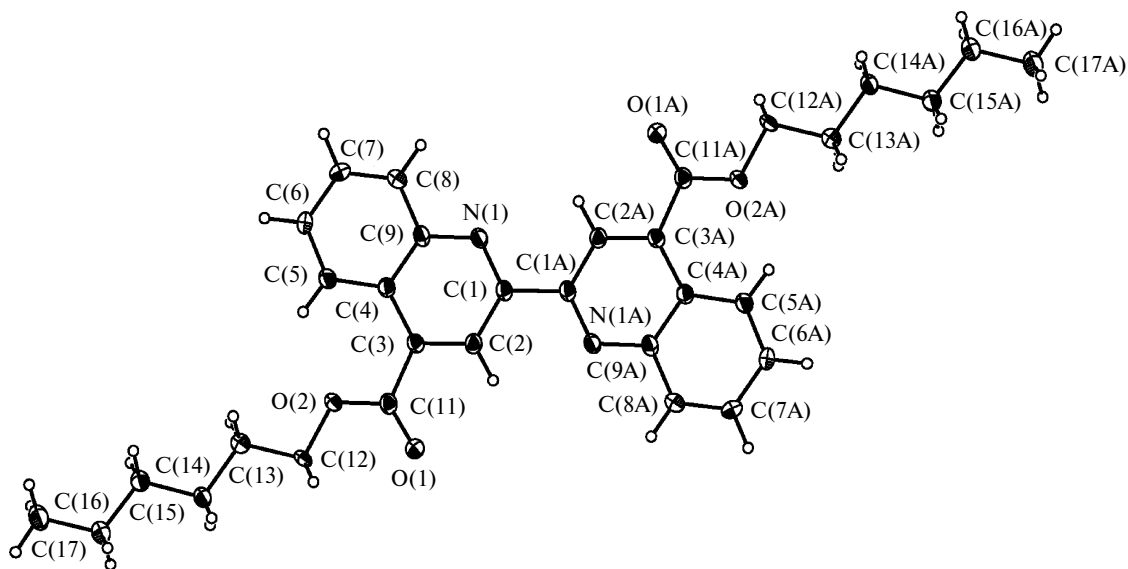| Parameter	1	2
Molecular formula	$C_{32}H_{36}N_2O_4$	$C_{64}H_{72}Cl_2Cu_2N_4O_8$
Molecular weight	512.63	1223.24
T/K	100	100
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\text{-}1$
Z ($Z´$)	2 (1´)	1 (0.5)
$a/Å$	8.2391(14)	8.3100(13)
$b/Å$	16.767(4)	13.484(2)
$c/Å$	9.618(3)	14.907(4)
α/deg	90.00	113.011(6)
β/deg	94.669(8)	102.776(5)
γ/deg	90.00	99.724(4)
$V/Å^3$	1324.3(6)	1437.4(5)
$d_{calc}/g\ cm^{-3}$	1.286	1.413
μ/cm^{-1}	0.85	8.93
$F(000)$	548	640
$2\theta_{max}/deg$	54	54
Number of measured reflections	6578	9708
Number of independent reflections	2973	6204
Number of reflections with $I > 2\sigma(I)$	1464	4143
Number of refined parameters	173	363
R_1	0.0565	0.0482
wR_2	0.1437	0.1073
GOF	0.914	0.953
Residual electron density /e·$Å^{-3}$, ρ_{max}/ρ_{min}	0.250/−0.241	0.459/−0.362

Fig. 1. Molecular structure of compound **1** with thermal ellipsoids ($p = 50\%$).

atom at the C(5) atom. The hexyl substituent has a planar zigzag conformation; the C—C—C—C torsion angles vary in the range of 174—177°. In the crystals, molecules **1** are involved not only in weak intermolecular C—H...π and C—H...O interactions but also in interactions between the π system of the heterocycle and the C=O bond with the C(6)...C(11) distance ($1 - x, 1 - y, 2 - z$) equal to 3.326(1) Å.

Complex **2** of ligand **1** with copper(I) chloride was synthesized by refluxing the reagents in a ratio of 1 : 1 in EtOH in the presence of an excess of hydroxylamine and ammonia. The recrystallization of the product from EtOH afforded small needle-like crystals suitable for X-ray diffraction. According to the X-ray diffraction data, the crystal structure of **2** consists of the dinuclear complexes [L$_2$Cu$^I_2$(μ-Cl)$_2$] containing Cu$_2$(μ-Cl)$_2$ clusters (see Tables 1 and 2, Fig. 2). Selected geometric parameters of the biquinoline ligand in complex **2** are virtually equal to those of **1**. The fragments of two biquinoline ligands linked together by the four-membered metallocycle Cu$_2$Cl$_2$ are coplanar but are shifted with respect to each other in such a way that they form a ladder motif with the distance between the planes equal to 1.95 Å. This shift is apparently associated with the tendency to reduce the steric repulsion between the hydrogen atoms of adjacent ligands (analogous ladder structures were found in the complexes of biq with nickel(II)[29] and manganese(II)[30] chlorides). The five-membered chelate ring adopts an envelope conformation with the copper atom deviating from the mean N(1)C(1)C(10)N(2) plane by 0.32 Å. As opposed to **1**, the ester groups form intramolecular C—H...O contacts not only with the hydrogen atom at C(5) but also with the hydrogen atom at C(11). In the crystals, molecules **2** are linked together through relatively strong stacking interactions (the shortest C(7)...C(18) distance is 3.27 Å,

Fig. 3) to form chains along the crystallographic axis *a*. In turn, the chains are linked together by intermolecular C=O...π interactions like those observed in **1** and by H...Cl and H...O interactions to form a three-dimensional framework.

A comparison of the single-crystal X-ray diffraction data and the X-ray powder diffraction data for complex **2** showed that the single crystals and the major phase of the product are identical in composition. Hence, the synthesis according to the above-described procedure affords only complex **2**.

Table 2. Selected bond lengths (*d*) and bond angles (ω) in the structure of **2**

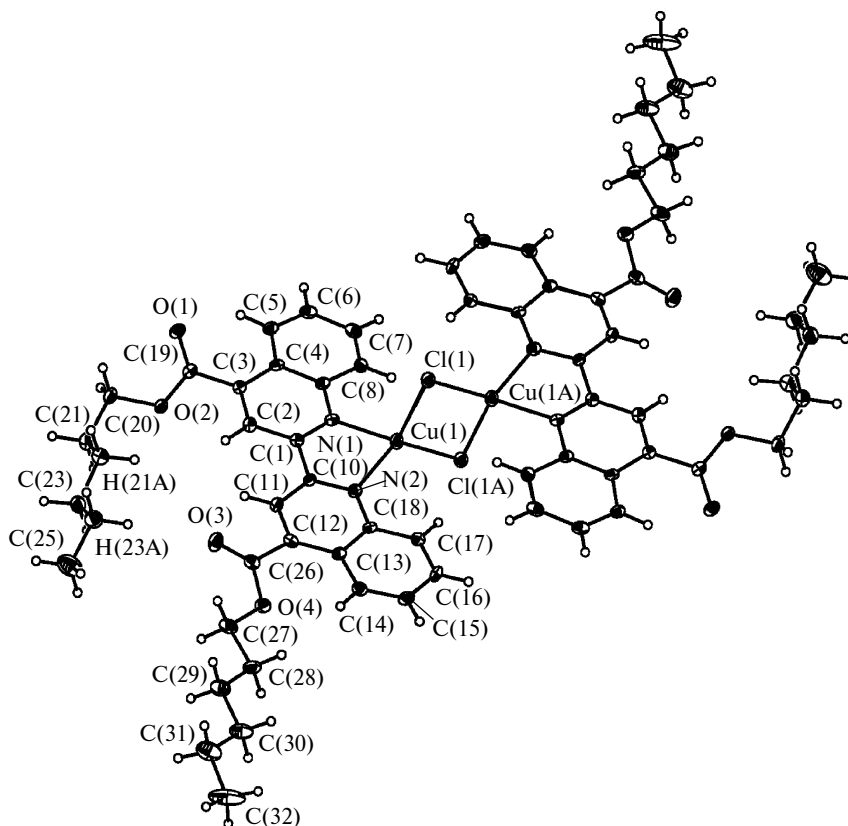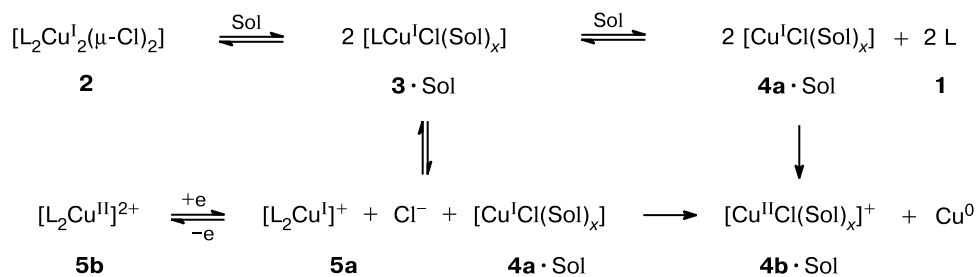| Parameter	Value
Bond length	*d*/Å
Cu(1)—N(1)	2.054(2)
Cu(1)—N(2)	2.068(2)
Cu(1)—Cl(1A)	2.2781(9)
Cu(1)—Cl(1)	2.3932(10)
Angle	ω/deg
N(1)—Cu(1)—N(2)	79.19(10)
N(1)—Cu(1)—Cl(1A)	128.24(7)
N(2)—Cu(1)—Cl(1A)	125.82(7)
N(1)—Cu(1)—Cl(1)	108.76(7)
N(2)—Cu(1)—Cl(1)	112.67(7)
Cl(1A)—Cu(1)—Cl(1)	101.30(3)
Cu(1A)—Cl(1)—Cu(1)	78.70(3)
C(1)—N(1)—Cu(1)	114.40(2)
C(9)—N(1)—Cu(1)	126.07(19)
C(10)—N(2)—Cu(1)	114.00(2)
C(18)—N(2)—Cu(1)	126.20(2)

Fig. 2. Molecular structure of **2**.

The hydrophobic hexyl "tails" are responsible for the good solubility of compound **2** in organic solvents. However, this factor is substantially reduced by the stacking interactions between the aromatic rings. Thus, complex **2** is very poorly soluble in chlorine-containing solvents, acetonitrile (AN), and alcohols and is slightly better soluble in dimethylformamide (DMF) and *N*-methyl-2-pyrrolidone (NMP).

The dissolution of complexes of type **2** can occur in several steps (Scheme 2). First, the dissolution of the complex $[L_2Cu^I_2(\mu\text{-Cl})_2]$ is not accompanied by a change in its composition. Second, the competition of the coordinating solvent with the bidentate ligands would be expected to give rise to the mononuclear species $[LCu^ICl(Sol)_x]$ (**3·Sol**) and even lead to the complete dissociation of the complex to form solvated copper(I) chloride (**4a·Sol**) and free ligand **1**. For the copper complexes with biq and phen, the ligand metathesis giving a two-ligand complex and solvated copper(I) halide was documented.[27,28] In some solvents, monovalent copper chloride (**4a·Sol**) can undergo disproportionation to copper(II) chloride (**4b·Sol**) and elemental copper Cu⁰. The oxidation of the copper(I) complex $[L_2Cu]^+$ (**5a**) to the copper(II) complex $[L_2Cu]^{2+}$ (**5b**), which is not accompanied by a change in its composi-

Scheme 2

$$[L_2Cu^I_2(\mu\text{-Cl})_2] \underset{}{\overset{Sol}{\rightleftharpoons}} 2\,[LCu^ICl(Sol)_x] \underset{}{\overset{Sol}{\rightleftharpoons}} 2\,[Cu^ICl(Sol)_x] + 2\,L$$

$$\textbf{2} \qquad\qquad \textbf{3}\cdot Sol \qquad\qquad \textbf{4a}\cdot Sol \qquad \textbf{1}$$

$$[L_2Cu^{II}]^{2+} \underset{-e}{\overset{+e}{\rightleftharpoons}} [L_2Cu^I]^+ + Cl^- + [Cu^ICl(Sol)_x] \longrightarrow [Cu^{II}Cl(Sol)_x]^+ + Cu^0$$

$$\textbf{5b} \qquad\qquad \textbf{5a} \qquad\qquad \textbf{4a}\cdot Sol \qquad\qquad \textbf{4b}\cdot Sol$$
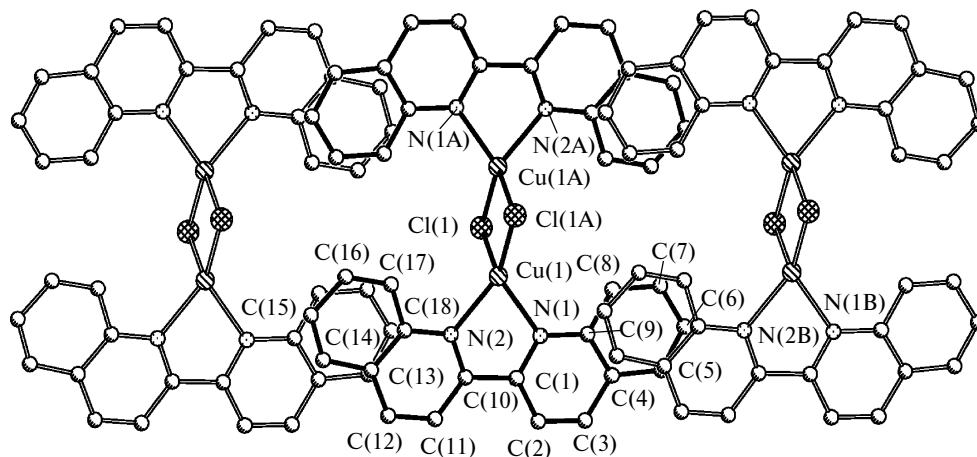
Sol is the solvent

Fig. 3. Stacking interactions between the carbocyclic moieties of the quinoline ligands in the crystal structure of **2**.

tion, can occur both under electrochemical conditions and in the presence of atmospheric oxygen (see Scheme 2).

In the present study, the behavior of complex **2** in solution was investigated by UV—Vis spectroscopy, cyclic voltammetry, and electrospray ionization mass spectrometry (ESI-MS). The ^{1}H NMR spectra provide little information because of the low solubility of the complex and the presence of paramagnetic impurities.

Mass spectrometry. The ESI-MS data obtained in the positive ion mode are presented in Table 3. The assignment of the peaks was made based on the character of the molecular mass distribution of the corresponding ions. The spectra of all solutions show the major peak at m/z 1087.5 assigned to the $[L_2Cu]^+$ ion (**5a**). The involvement of the solvent molecules in the equilibrium is evidenced by the fact that the spectrum contains the $[LCu(Sol)]^+$ ions (**3·Sol − Cl**), whose intensity varies from 10 to 20% of the major signal. In addition, the spectra recorded in DMF and NMP contain ion peaks corresponding to the protonated ligand, whose intensity increases with time. The signal of the $[L_2Cu_2Cl]^+$ ion (**2 − Cl**) assigned to the dinuclear complexes is observed in a solution of the complex in acetonitrile and in a freshly prepared solution in NMP. The intensity of this peak varies from 5 to 10% of the intensity of the major ion peak. It should be noted that the peak corresponding to the complex with the composition $[L_2Cu]^+$ (**5a**) is absent in the spectrum recorded after the mixing of acetonitrile solutions of ligand **1** and $[Cu(BF_4)_2 \cdot (H_2O)_x]$, and the spectrum shows only the peak of the $[LCuH_2O]^+$ ion that is formed as a result of the reduction of the complex under the conditions of the analysis.

Spectrophotometry. Solutions of complex **2** in EtOH, MeOH, DMF, NMP, and AN are characterized by the violet color, which is attributed to a relatively intense metal-to-ligand charge-transfer band (MLCT,[27,28] Table 4). However, the stability of the color and, consequently, of

the species responsible for this color is different in different solvents. Thus, no noticeable changes in the spectra are observed in alcohols during several hours. In the other solvents, the color of the complex changes with time from violet to pale-yellow (Fig. 4). The rate of the change in the color decreases in the series NMP > DMF > AN.

The spectrophotometric titration of a solution of the ligand with a solution of copper(I) chloride showed the presence of several types of species (Fig. 5). In the presence of a ninefold excess of copper(I) chloride, the major absorption band is observed at 445 nm, and the band at 580 nm has a low intensity. In the presence of an excess of the ligand, these absorption bands are similar in intensity. Based on the published data,[9,28,31,32] the band at 580 nm should be assigned to MLCT of the tetrahedral mononuclear complex $[L_2Cu]Cl$ ([**5a**]Cl). Taking into account

Table 3. Composition of the solutions of complex **2** determined by ESI-MS

Solvent	m/z [Ion]			
NMP	1187.4 $[L_2Cu_2Cl]^+$	1087.5 $[L_2Cu]^+$	674.3 $[LCu(NMP)]^+$	513.2 $[LH]^+$
MeOH	—	1087.5 $[L_2Cu]^+$	—	—
AN*	1187.4 $[L_2Cu_2Cl]^+$	1087.5 $[L_2Cu]^+$	616.2 $[LCu(AN)]^+$	—
DMF	—	1087.5 $[L_2Cu]^+$	—	513.2 $[LH]^+$
AN**	—	—	593.2 $[LCuH_2O]^+$	—

* After storage in air, a peak of the $[LCuCl]^+$ ion corresponding to the Cu^{II} complex appeared. This peak (along with the peak of the monovalent copper complex $[L_2Cu]^+$) is the major peak in the solution prepared by mixing L and CuCl$_2$ in AN.

** In the study, a solution prepared by mixing solutions of $[Cu(BF_4)_2 \cdot (H_2O)_x]$ and ligand **1** was used.
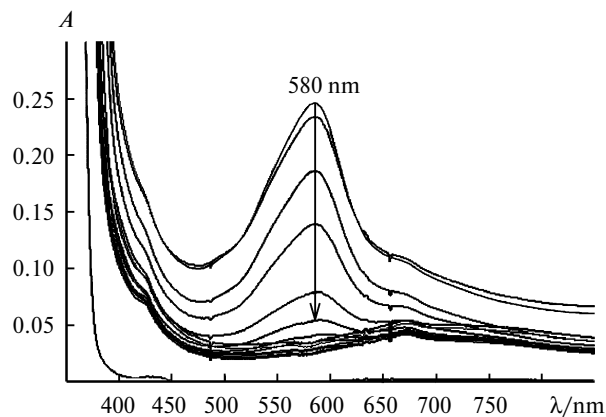
Fig. 4. Time evolution of the UV—Vis spectrum of a solution of complex **2** in NMP (changes in the color during 10 min).

this fact, the band at 445 nm can be assigned to the dinuclear complex [$L_2Cu_2Cl_2$] (**2**). A similar value was reported in the study[27] for the dinuclear complex of CuCl with phen. The absence of isosbestic points in Fig. 5 is indicative of a complex system of equilibria in solution, which is consistent with Scheme 2.

Cyclic voltammetry. The electrochemical behavior of complex **2** was studied in two solvents (AN and NMP). Figure 6, *a* shows the cyclic voltammogram of complex **2** in AN.

Two quasi-reversible peaks are observed in the anodic scan at $E = 0.74$ and 1.15 V (see Fig. 6, *a*). The oxidation of the complex occurs at a relatively high potential (0.74 V), which is characteristic of sterically crowded tetraaza-coordinated Cu^I complexes.[26,31,33] The second oxi-

Table 4. UV—Vis data for solutions of complex **2** and related compounds

Complex	Solvent	λ_{max}/nm	Reference
2	AN	445, 580	*
	EtOH	580	*
	NMP	445 (sh) 580	*
	Me_2CO	580	*
[L_2Cu]BF_4	NMP	580	*
[(biq)$_2Cu$]BF_4	DMF	524, 552	31
[(biq)$_2Cu$]ClO_4	AN	546	9
[(biq)$_2Cu$]X	Me_2CO	545	28
(X = Cl, Br, I)	EtOH	545	
[(4-biq-COONa)$_2Cu$]Cl**	H_2O	565	32
[(phen)CuCl]$_2$	Me_2CO	445	27

* The present study.
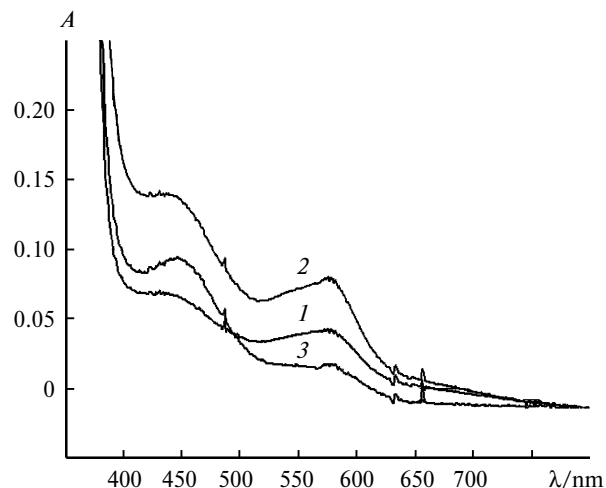** 4-biq-COONa is 2,2′-biquinoline-4,4′-dicarboxylic acid disodium salt.

Fig. 5. Spectrophotometric titration of a solution of **1** with a solution of copper chloride in AN at different ligand-to-metal ratios: 1 : 4 (*1*), 1 : 1 (*2*), and 9 : 1 (*3*).
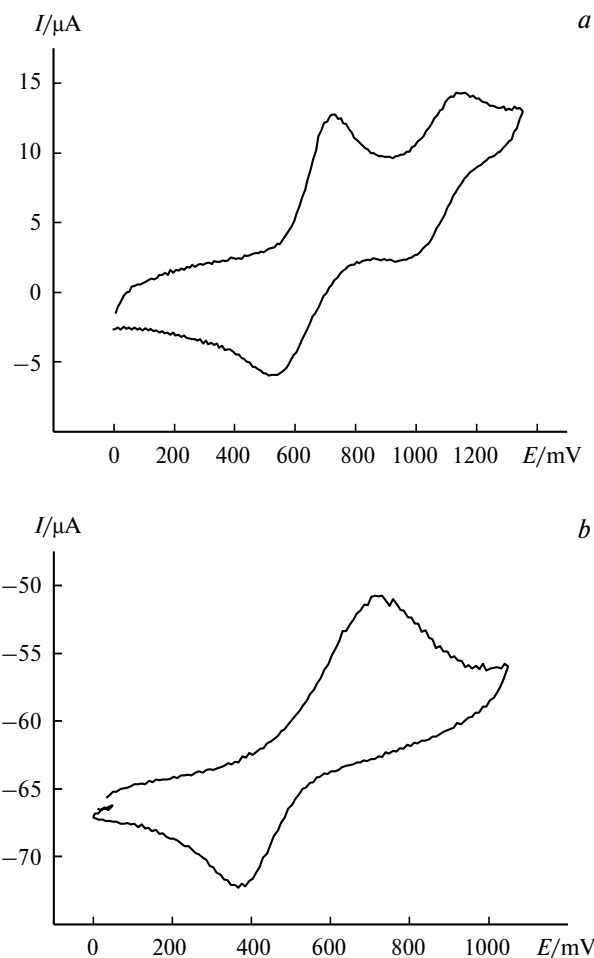

Fig. 6. Cyclic voltammograms of complex **2** in MeCN (*a*) and NMP (*b*) (Pt, 0.05 *M* Bu$_4NBF_4$, 100 mV s^{-1}, with respect to Ag/AgCl/KCl).

dation peak at $E = 1.15$ V can be assigned to either the oxidation of the second copper center in bridged dinuclear complex **2** (similar examples were published in the literature[27]) or the transformation products of **2** in solution (see Scheme 2). Thus, the chloride-bridged copper(I) phen complexes in Me_2CO exhibit two reversible peaks with the same current intensities during electrochemical oxidation;[27] the nature of the peaks was explained by the successive oxidation of the copper centers in the bridged dinuclear complexes stable in this medium.

In our study, the current of the first oxidation peak is two times higher than that of the second peak (see Fig. 6, *a*). This experimental fact is inconsistent with the successive oxidation of two copper atoms in the bridged dinuclear complexes; otherwise, the peaks should be equal in height. In our opinion, bridged dinuclear copper complex **2** undergoes dissociation upon dissolution in AN (see Scheme 2). In the first step, the chloride bridges in complex **2** are cleaved to form the complex **3 · Sol**, in which the chloride ion and the solvent molecules are exchanged for the biquinoline ligand (ligand metathesis) to form mononuclear copper bis-biquinoline complex **5a** and the complex **4a · Sol**. It is known[34] that CuCl is unstable in AN and readily undergoes disproportionation to copper metal and copper(II) chloride. The control experiment on the electrochemical behavior of $CuCl_2$ in AN showed the presence of a reversible oxidation peak at $+1.15$ V corresponding to the Cu^{II}/Cu^{III} redox transition. Hence, the reversible oxidation of complex **5a** to complex **5b** occurs at $E = +0.74$ V (see Scheme 2), and the reversible oxidation of $CuCl_2$ that is formed in solution occurs at $+1.15$ V (**4b**, see Fig. 6, *a*).

The stoichiometry of the above-considered steps suggests that the current of the second oxidation peak should be two times smaller than that of the first peak, which was confirmed experimentally (see Fig. 6, *a*). The ratio of the heights of the direct and reverse peaks for the first redox transition is close to the unity, which indicates that complex **5b** is stable on the cyclic voltammetry time scale. The potential difference between the direct and reverse oxidation peaks is 150 and 105 mV for the first and second oxidation peaks, respectively. This difference can be attributed to a change in the geometry of the coordination unit attendant on the redox transition.

The formation of the tetrahedral Cu^I complex containing two biquinoline ligands in the coordination environment of the copper ion (**5a**) in solution is in good agreement with our previous data.[35] The anodic dissolution of copper in the presence of diester of 2,2´-biquinolyl-4,4´-dicarboxylic acid (4-biq-COOR) affords the complex [(4-biq-COOR)$_2$Cu^I]BF$_4$ (**5a · BF$_4$**), whose structure was established by different physicochemical methods (UV—Vis, MALDI-TOF mass spectrometry, and cyclic voltammetry). The cyclic voltammogram of this complex shows an oxidation peak in the anodic scan at the same

potential ($E = 0.75$ V)[35] as that observed for a solution of **2** in AN.

The electrochemical behavior of complex **2** was studied also in NMP. The corresponding cyclic voltammogram is shown in Fig. 6, *b*.

In the anodic potential scan, only one quasi-reversible peak is observed at $E = 0.74$ V, which corresponds to the transition **5a**$\leftrightarrows$**5b**. The reverse reduction peak is seen on the reverse scan (the current ratio of the direct and reverse waves $I_c/I_a = 0.7$). This is indicative of the lower stability of the oxidized form of the complex in NMP compared to AN. The potential difference between the direct and reverse oxidation peaks is relatively large (320 mV). This is evidence that the electron transfer is followed by the chemical step or an essential structural reorganization of the complex.[36] Apparently, the oxidation of the copper complex in NMP is accompanied by the elimination of one of the biquinoline ligands from complex **5b** and the stabilization of the resulting complex **3 · Sol** by NMP molecules. Previously, our calculations[37] of the energies of the formation of the complexes [(biq)$_2$Cu]$^{2+}$ and [(biq)Cu(NMP)$_2$]$^{2+}$ by the DFT method have shown that these energies are similar in the magnitude (-458.6 and -454.8 kcal mol^{-1}, respectively).

Therefore, the above data suggest that the dinuclear structure of chloride-bridged complex **2** is destroyed both in NMP and AN to form tetrahedral bis-biquinoline complex **5a** as the major product (see Scheme 2). The main difference in the electrochemical behavior of complex **2** in NMP and AN is that the oxidation peak of $CuCl_2$ is absent in the former case. This is attributed to the fact that CuCl that is formed in NMP in the course of the ligand metathesis does not undergo disproportionation; instead, it precipitates due to the low solubility in this solvent. The fact that dinuclear complex **2** is not observed in electrochemical experiments is associated with that the electrochemical experiments were carried out in the presence of a 100-fold excess of the supporting electrolyte (tetrabutylammonium tetrafluoroborate), which apparently additionally facilitates the cleavage of the chloride bridges in complex **2**.

To summarize the results obtained with the use of the above-described three methods, the following conclusions can be drawn.

(1) The L/Cu/Cl system crystallizes from EtOH and AN only as dinuclear molecules **2**.

(2) After the dissolution of complex **2** in AN and NMP, the solutions contained the [L$_2$Cu$_2$(μ-Cl)$_2$] (an absorption band at 445 nm; the presence of the [L$_2$Cu$_2$Cl]$^+$ ion in the mass spectrum), [L$_2$Cu]Cl (an absorption band at 580 nm; the presence of the [L$_2$Cu]$^+$ ion in the mass spectrum), [LCuCl(Sol)] (the presence of the corresponding ions in the mass spectra), and [CuCl(Sol)] (observed only in AN) species.

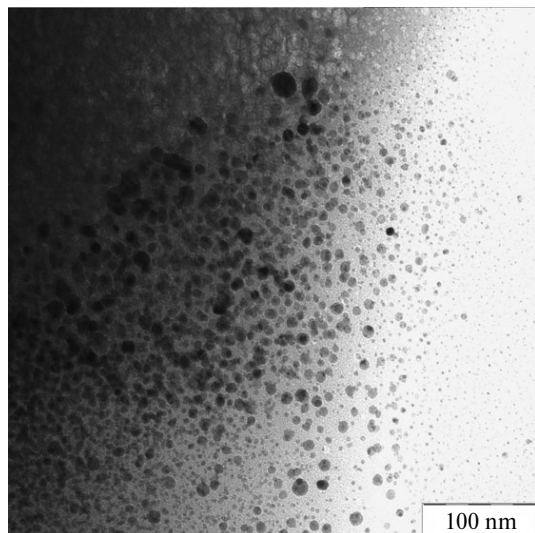(3) Solutions of complex **2** in alcohols and DMF contain only [L$_2$Cu]Cl and [CuCl(Sol)].

Fig. 7. Electron photomicrograph of the sample prepared by the evaporation of an ethanolic solution of **2**.

(4) In EtOH, AN, and DMF, the [CuCl(Sol)] species undergo disproportionation to [Cu^{II}Cl(Sol)] and Cu^0. Copper nanoparticles in the samples prepared by the evaporation of solutions of **2** can be observed with a transmission electron microscope (Fig. 7). In NMP, the [CuCl(Sol)] species are insoluble and precipitate without disproportionation.

Experimental

The electrochemical oxidation and reduction potentials were measured on an IPC_Win digital potentiostat/galvanostat connected to a personal computer. The voltammograms were recorded using 0.05 *M* Bu$^n_4$NPF$_6$ as the supporting electrolyte in AN and NMP at 20 °C in a 8 mL electrochemical cell. Oxygen was removed from the cell by purging with dry argon. The voltammograms were recorded by cyclic voltammetry on a stationary platinum electrode at different potential scan rates. Platinum wire served as the auxiliary electrode, and a saturated silver chloride electrode was used as the reference electrode (the potential *vs.* Fc/Fc$^+$ is −0.48 V in NMP).

The X-ray diffraction studies of compounds **1** and **2** were carried out on a SMART APEX II CCD diffractometer (Mo-Kα radiation, graphite monochromator, 120(2) K, ω-scanning technique) The structures were solved by direct methods and refined anisotropically by the full-matrix least-squares method based on F^2_{hkl}. The hydrogen atoms were positioned geometrically and refined isotropically using a riding model. The principal crystallographic parameters and the refinement statistics are given in Table 1. All calculations were carried out with the use of the SHELXTL PLUS program package.

The solvents were purified according to standard procedures. Commercially available starting compounds were used without additional purification.

2,2´-Biquinoline-4,4´-dicarboxylic acid. Isatin (73.5 g, 0.5 mol), acetoin (14.08 g, 0.16 mol), and a 33% potassium hydroxide solution (400 mL) were placed in a one-neck round-bottom flask. The solution was refluxed for 24 h. The resulting salt was filtered off, washed with an alkali solution, dissolved in water, and acidified with a weak hydrochloric acid solution. The crystals that formed were filtered off, washed with water, dried, and purified by reprecipitation from a potassium hydroxide solution. The yield was 78%, m.p. 300—301 °C (*cf.* lit. data[38]: m.p. 300—302 °C).

Dihexyl 2,2´-biquinoline-4,4´-dicarboxylate (1). 2,2´-Biquinoline-4,4´-dicarboxylic acid (1 g) and *n*-hexanol (10 mL) were placed in a one-neck round-bottom flask equipped with a reflux condenser, and then concentrated sulfuric acid (2 mL) was added dropwise. The reaction mixture was refluxed for 1.5 h, cooled, and poured into water (100 mL). The precipitate that formed was filtered off, washed with water, dried, and twice recrystallized from EtOH. The yield was 55%, m.p. 110 °C (*cf.* lit. data[32]: m.p. 115 °C). Attempts to isolate ester **1** in the analytically pure form failed, and it was used for the synthesis of complex **2** without additional purification.

Reaction of compound 1 with copper(I) chloride. A solution of hydroxylamine hydrochloride (3 g, 43 mmol) in water (15 mL) was brought to pH = 5.5 with a 10% ammonia solution. Then EtOH (50 mL) and CuCl (0.27 g, 2.7 mmol) were added. The resulting solution was added to a solution of dihexyl 2,2´-biquinoline-4,4´-dicarboxylate (**1**) (1.4 g, 2.9 mmol) in EtOH (150 mL), and the mixture was refluxed for 0.5 h. Then EtOH was distilled off and the solution was cooled. The precipitate that formed (dark sparkling crystals) was filtered off, washed three times with EtOH, and dried. The yield of complex **2** was 1.5 g (91%). Found (%): C, 62.63; H, 6.01; N, 4.59. C$_{32}$H$_{36}$Cl$_2$CuN$_2$O$_4$. Calculated (%): C, 62.70; H, 5.88; N, 4.47.

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