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Syntheses, Structures, and Geometric and Spectral Characteristics of the Hexachlorodicuprate(II) Complexes with the Protonated 4-Azafluoren-9-one Derivatives: The Crystal and Molecular Structures of Bis(4-Azafluoren-9-onium) Hexachlorodiaquadicuprate(II) Dihydrate

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Abstract—Three complexes containing hexachlorodicuprate(II) anions and protonated 4-azafluorenone derivatives as counterions were isolated. The crystal and molecular structures of 4-azafluoren-9-one, $(HL^1)_2[\{CuCl_2(H_2O)\}_2(\mu\text{-}Cl)_2] \cdot 2H_2O$ (L^1), and spectral characteristics of the complexes were determined. Relationships relating the degree of distortion of the crystal structure of the hexachlorodicuprate(II) anions to the spectral characteristics of the compounds were proposed on the basis of the experimental and published data.

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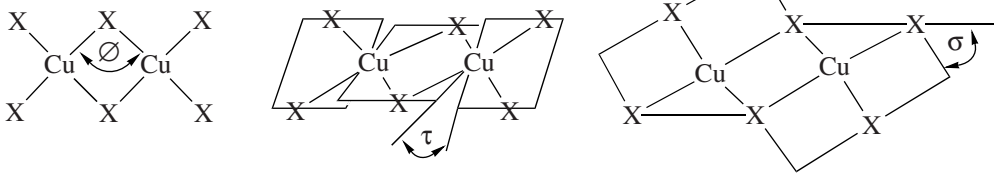
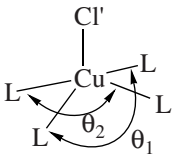
INTRODUCTION

In this work, we continue a series of studies of the anionic chloro- and bromocuprate(II) complexes containing the organic nitrogen-containing bases as counterions [1–4].

The symmetric dibridge halogencuprate structure is based on the $Cu_2X_6^{2-}$ dimer having three main geometric configurations [5]:



The copper atom is characterized by the attachment of an additional ligand to form pentacoordinate complexes with the geometry of a square pyramid or trigonal bipyramid. The degree of distortion of the environment of the pentacoordinate copper is characterized by the θ *trans* angles [5]:



$\Delta = \theta_2 - \theta_1$

If the structure belongs to the type of a square pyramid, $\theta_1 \approx \theta_2$. For the trigonal bipyramidal configuration, the θ angles range as follows: $\theta_1 \longrightarrow 120°$, $\theta_2 \longrightarrow 180°$, and $\Delta = \theta_2 - \theta_1 = 60°$.

The present work is devoted to the synthesis of the hexachlorocuprate(II) complexes with 4-azafluoren-9-one (**L[1]**) (**I**), 1-ethyl-3-methyl-4-azafluoren-9-one (**L[2]**) (**II**), and 1-amino-4-azafluoren-9-one (**L[3]**) (**III**) and the study of their structures and spectral characteristics. The experimental and literature data on the crystalline and spectral properties of the hexachlorodicuprate(II) anions were generalized, which made it possible to construct relationships that can be used for the estimation of the degree of distortion of the coordination poly-

Table 1. Chemical analysis results for complexes **I–III**

Complex	Empirical formula	FW	Content (calculated/found), %			
			C	N	Cu	Cl
$(HL^1)_2[\{CuCl_2(H_2O)\}_2(\mu\text{-}Cl)_2] \cdot 2H_2O$ (**I**)	$C_{24}H_{24}N_2OCu_2Cl_6$	776.27	37.13/37.44	3.61/3.64	16.37/16.63	27.40/27.68
$(HL^2)_2[Cu_2Cl_6]$ (**II**)	$C_{30}H_{28}N_2O_2Cu_2Cl_6$	788.37	45.71/45.17	3.55/3.54	16.12/16.38	26.98/27.23
$(HL^3)_2[Cu_2Cl_6(H_2O)_2]$ (**III**)	$C_{24}H_{22}N_4O_4Cu_2Cl_6$	770.27	37.42/37.62	7.27/7.33	16.50/16.47	27.62/27.05

hedron of copper(II) by the spectral characteristics of the isolated polycrystalline complexes.

EXPERIMENTAL

Synthesis of complexes I–III. A weighed sample of an organic base (5×10^{-4} mol) was dissolved in a minimum volume of ethanol. An ethanolic solution of copper(II) chloride ($c_{Cu^{2+}} = 2.5 \times 10^{-3}$ mol/l) was added with stirring to the resulting solution, and a concentrated solution of HCl was added dropwise to pH 2.5–2. The reaction mixture was stored in a water bath for 30 min at 50°C. The precipitates formed after cooling were filtered off and dried over P_2O_5 to a constant weight. The yield was 45–50%. The crystals of complexes **I–III** are red-brown and unstable in polar solvents. Their individual and single-phase character was proved by the method of crystal optics. The compositions of the isolated compounds were determined by elemental analyses (Table 1). Single crystals of compound **I** appropriate for X-ray diffraction analysis were isolated by recrystallization from acidified ethanol.

X-ray diffraction analysis was carried out on an Enraf-Nonius CAD-4 automated four-circle diffractometer (MoK_α radiation, graphite monochromator, $\theta/2\theta$ scan mode, $\theta_{max} = 25.97°$). The total number of measured independent reflections was 2925 in the I index range: $-9 \le h \le 0$, $-10 \le k \le 10$, $-13 \le l \le 13$. In calculations, 2211 independent reflections with $I > 2\sigma(I)$ were used. The structure was solved by a direct method and refined by the least-squares method in the full-matrix anisotropic approximation for non-hydrogen atoms. The coordinates of hydrogen atoms were revealed from the difference Fourier synthesis and included into the refinement with the stationary coordinates and isotropic thermal parameters. The final R factor values were $R = 0.031$, $wR_2 = 0.080$ (for all reflections with $I > 2\sigma(I)$), the goodness-of-fit being 0.979. All calculations were performed by the SHELX-97 program package [6].

Table 2. Selected bond lengths and bond angles in structure **I***

Bond	d, Å	Angle	ω, deg
Cu(1)–O(3)	1.9548(17)	O(3)Cu(1)Cl(2)	90.89(6)
Cu(1)–Cl(2)	2.2652(9)	O(3)Cu(1)Cl(3)	168.68(6)
Cu(1)–Cl(3)	2.2738(8)	Cl(2)Cu(1)Cl(3)	92.58(3)
Cu(1)–Cl(3)$^{\#1}$	2.3072(10)	O(3)Cu(1)Cl(3)$^{\#1}$	87.99(6)
Cu(1)–Cl(1)	2.5926(11)	Cl(2)Cu(1)Cl(3)$^{\#1}$	162.49(3)
O(1)–C(11)	1.210(4)	Cl(3)Cu(1)Cl(3)$^{\#1}$	85.46(3)
N(1)–C(4)	1.329(3)	O(3)Cu(1)Cl(1)	91.59(7)
N(1)–C(3)	1.349(3)	Cl(2)Cu(1)Cl(1)	96.48(4)
N(1)–H(1N)	0.95(4)	Cl(3)Cu(1)Cl(1)	98.72(4)
		Cl(3)$^{\#1}$Cu(1)Cl(1)	101.02(4)
		Cu(1)Cl(3)Cu(1)$^{\#1}$	94.54(3)
		H(21)O(2)H(22)	109(4)
		Cu(1)O(3)H(31)	120(3)
		Cu(1)O(3)H(32)	117(2)
		H(31)O(3)H(32)	114(4)

* Symmetry transformations: $^{\#1}$ $-x + 1, -y + 1, -z + 3$.

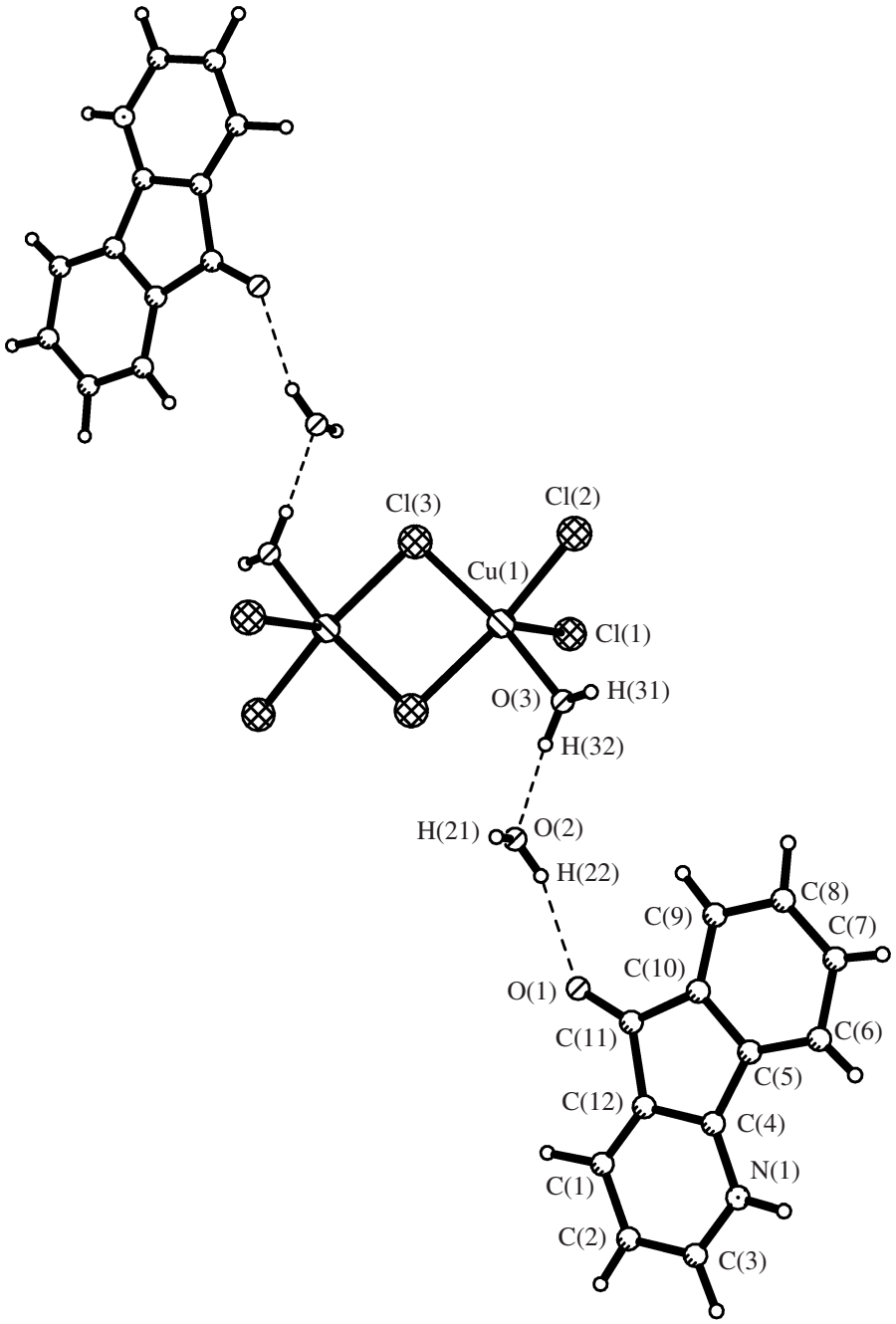


Fig. 1. Structure of the$(HL^1)_2[\{CuCl_2(H_2O)\}_2(\mu\text{-}Cl)_2] \cdot 2H_2O$ compound (**I**).

The crystals of compound **I** are triclinic: space group $P\bar{1}$, $a = 7.681(2)$, $b = 9.112(2)$, $c = 11.550(2)$ Å, $\alpha = 80.86(3)°$, $\beta = 76.17(3)°$, $\gamma = 74.82(3)°$, $V = 753.5(3)$ Å^3, $\rho_{calcd} = 1.711$ g/cm^3, $Z = 2$.

Selected bond lengths and bond angles in structure **I** are listed in Table 2. The coordinates of atoms and other parameters of structure **I** were deposited with the Cambridge Structural Database (no. 681 143).

The electronic absorption spectra of complexes **I–III** were recorded in the interval from 50000 to 15000 cm^{-1} on a Specord UV-VIS spectrometer (suspensions in Nujol).

RESULTS AND DISCUSSION

According to the X-ray diffraction data, the structural units of complex **I** are the $[Cu_2Cl_6(H_2O)_2]^{2-}$ anion,

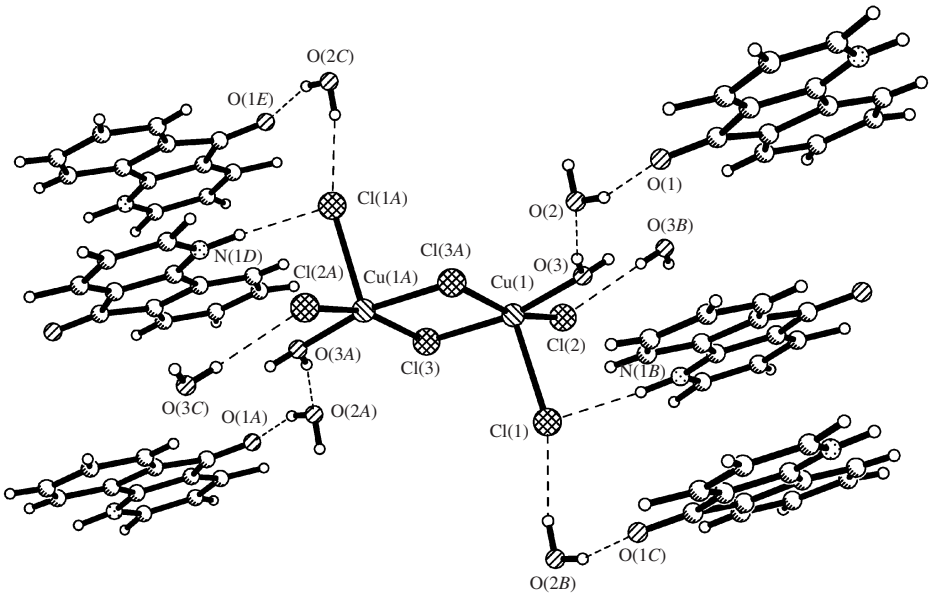


Fig. 2. Fragment of the molecular structure of compound **I** and the system of hydrogen bonds in the crystal structure.

$(HL^1)^+$ cations, and water molecules (Fig. 1). In the anion, the copper(II) atoms are linked by two bridging chlorine atoms (the CuClCu angle is 94.56°). The copper(II) atom is coordinated by two terminal (t) and two bridging (b) chlorine atoms and the oxygen atom of the water molecule. The $CuCl_4(H_2O)$ polyhedron (Table 2) is a square pyramid (SP) in which the Cl atom occupies the axial position. Three Cl atoms and the $O(H_2O)$ atom lie in the base plane. The average deviation of these atoms from the plane of the pyramid base is 0.08 Å, and the Cu atom is shifted by 0.27 Å from this plane to the axial vertex. The average statistical $Cu–Cl_b$ distance is 2.291(1) ± 0.017 Å. The $Cu–Cl(1)_t$ axial bond (2.593(1) Å) is substantially (by 0.328 Å) longer than the $Cu–Cl(2)_t$ equatorial bond (2.265(1) Å). In the $[Cu_2Cl_6(H_2O)_2]^{2-}$ anion, the twist angle τ between the plane of the central (Cu_2Cl_2) and terminal ($CuCl_2O$) fragments is 20°. The shortest distances in the dimeric anion are Cl···Cl (3.11 Å) and Cu···Cu (3.37 Å).

The organic cation is a 4-azafluoren-9-one molecule protonated at the pyridinium nitrogen atom. The tricyclic framework is planar, and the bond lengths in compound **I** correspond to those in the structure of bis(4-azafluoren-9-onium) tetrabromocuprate(II) hydrate [3].

The organic cations and inorganic anions in crystal **I** are joined by hydrogen bonds OH···O into layers through the crystallization water molecules (Fig. 1). The shortest interdimeric distances are Cl–Cl (3.11 Å) and Cu–Cu (3.37 Å). The layers are joined by the N^+H···Cl and OH···Cl interionic hydrogen bonds (Fig. 2). The hydrogen bonding parameters are given in Table 3.

The electronic absorption spectra of the chlorocuprate complexes with the organic cations exhibit three main groups of absorption bands: the electron transitions of the organic cations (ligand bands), *d–d* transitions of Cu^{2+}, and the ligand-to-metal charge-transfer (LMCT) band [4].

An analysis of the literature data along with the present results (Table 4) make it possible to derive a satisfactory dependence of the position of the LMCT bands (Cl ⟶ Cu) in the absorption spectrum on the degree of distortion of the $Cu_2Cl_6^{2-}$ coordination polyhedron determined by the Δ value (the difference between two *trans* angles [5]), which changes from 0° in the SP (ν_{LMCT} = 19610–19900 cm^{-1}) to 60° in the trigonal bipyramid (TBP) (ν_{LMCT} = 23880–24390 cm^{-1}). In order to construct the relationships, we used our earlier results on the structural and spectral properties of the complexes $[(HL^4)_2Cu_2Cl_6]$ (**IV**), where L^4 is 1-amino-9-hydroxy-4-azafluorene [1], and $[(HL^5)_2Cu_2Cl_6] \cdot (HL^5)Cl$ (**V**), where L^5 is 3-amino-2-methyl-4H-pyrido[1,2-a]-pyrimidin-4-one [2], as well as the published data for the following compounds: $[([(HL^6)_2Cu_2Cl_6]$ (**VI**)), where L^6 is ethanolamine [7], $[([(HL^7)_2Cu_2Cl_6]$ (**VII**)), where L^7 is isopropylamine [8], and $[([(HL^8)_2Cu_2Cl_6]$ (**VIII**)), where L^8 is N,N'-dimethyl-4,4'-bipyridine [9].

The position of the LMCT bands in the absorption spectra of the dimeric anionic copper(II) complexes can serve as a characteristic of the degree of distortion of the $Cu_2Cl_6^{2-}$ coordination polyhedron (Fig. 3). The con-

Table 3. Hydrogen bonding geometry in structure **I**

Contact D–H···A	Position of A atom	Distance, Å			Angle DHA, deg
		D···A	H···A	D···H	
N(1)–H(1N)···Cl(1)	$1 - x, -y, 2 - z$	3.099(2)	2.16(4)	0.95(4)	174(3)
O(2)–H(21)···Cl(1)	$1 - x, y, z$	3.140(3)	2.29(4)	0.86(4)	170(3)
O(3)–H(31)···Cl(2)	$1 - x, -y, 3 - z$	3.081(2)	2.29(4)	0.81(4)	163(3)
O(2)–H(22)···O(1)	x, y, z	2.866(3)	2.10(5)	0.80(5)	161(5)
O(3)–H(32)···O(2)	x, y, z	2.651(3)	1.84(4)	0.83(4)	164(4)

structed plots consist of two linear sections with mutually inverse slopes. The points corresponding to the SP structures (Fig. 3a) lie in the ascending section (Δ from 4 to 6.5), whereas the descending section (Δ from 15 to 46) contain the points of the TBP structures (Fig. 3b). The Δ values for polycrystalline samples **II** and **III** lie

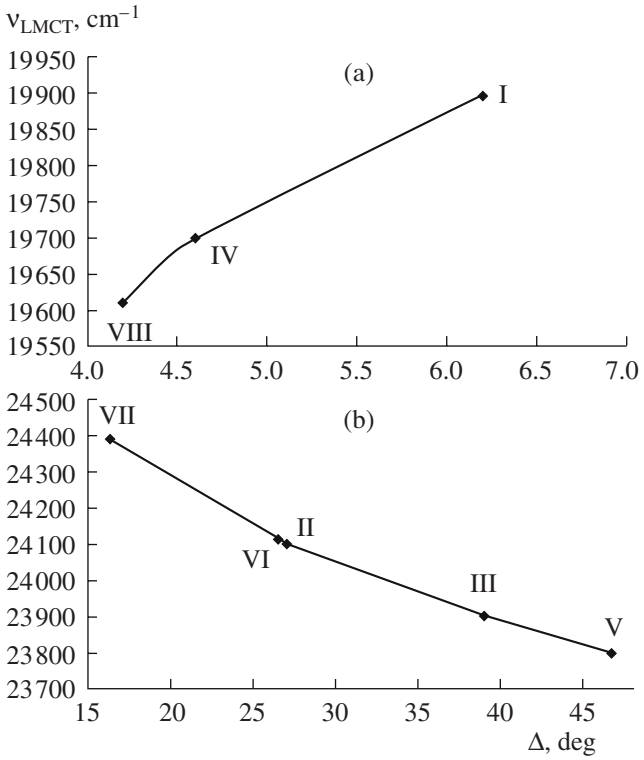


Fig. 3. Plots of the position of the LMCT bands vs. degree of distortion of the coordination polyhedron (Δ): (a) SP and (b) TBP.

Table 4. Degree of distortion of the coordination polyhedron (Δ) and the position of the LMCT (L ⟶ Cu) band in selected binuclear hexachlorodicuprate complexes

Complex	Coordination polyhedron	Δ, deg	ν_{LMCT}, cm^{-1}	Literature
I	SP	6.2	19900	This work
II	TBP	27*	24100	This work
III	TBP	39*	23900	This work
IV	SP	4.6	19700	[1]
V	TBP	46.6	23800	[2]
VI	TBP	26.5	24110	[7]
VII	TBP Flattened TBP	16.3	24390	[8]
VIII	SP	4.2	19610	[9]

* The values were obtained from the plot in Fig. 3.

at 27° and 39°, respectively and, therefore, we can assign them to the TBP structure.

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