Dinuclear and polynuclear transition metal complexes with macrocyclic ligands

6.* New dinuclear copper(II) complexes with macrocyclic Schiff bases derived from 4-*tert*-butyl-2,6-diformylphenol *

V. V. Roznyatovsky,[a]* *N. E. Borisova,*[a] *M. D. Reshetova,*[a] *Yu. A. Ustynyuk,*[a]*
G. G. Aleksandrov,[b] *I. L. Eremenko,*[b] *and I. I. Moiseev*[b]

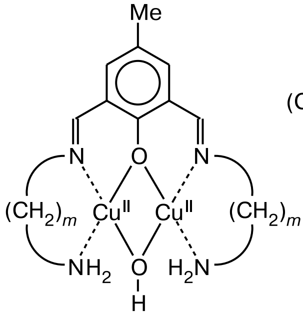
[a]*Department of Chemistry, Moscow State University,*
Leninskie Gory, 119992 Moscow, Russian Federation.
Fax: +7 (095) 939 2677. E-mail: yustynyuk@nmr.chem.msu.su
[b]*N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences,*
31 Leninsky prosp., 119991 Moscow, Russian Federation.
Fax: +7 (095) 954 1279. E-mail: ilerem@igic.ras.ru

New dinuclear complexes containing Cu^{II} atoms in the cavity of a macrocyclic Schiff base were prepared by template condensation of 4-*tert*-butyl-2,6-diformylphenol with 1,3-diaminopropane in the presence of Cu^{II} trimethylacetate and chloride as well as by extra-ligand exchange. The mononuclear Cu^{II} complex with two 1,3-diaminopropane molecules can serve as an intermediate in this template synthesis. The reaction of Cu^{II} trimethylacetate with the unsymmetrical macrocyclic Schiff base synthesized earlier afforded a new dinuclear copper(II) complex with the amine and imine nitrogen atoms in the coordination sphere. The structures of the new complexes were established by X-ray diffraction analysis and studied by the density functional theory (gradient-corrected PBE functional, TZ2p basis set).

Key words: copper(II) complexes with macrocyclic Schiff bases, X-ray diffraction analysis, density functional theory.

Dinuclear copper complexes attract attention as models of active centers of copper-containing enzymes (tyrosinase, hemocyanin, hemerythrin, cytochrome *c* oxidase, *etc.*[2,3]) and potential components of homogeneous catalytic systems.[4] Among these complexes, homodinuclear complexes, in which both copper atoms are located in the cavity of the macrocyclic ligand immediately adjacent to one another, are of particular interest. Complexes with macrocyclic Schiff bases derived from the condensation products of 4-substituted 2,6-diformylphenols and various diamines have received the most study.[5]

Condensation of the sodium salt of 2,6-diformyl-4-methylphenol with an excess of aliphatic diamines in the presence of copper(II) perchlorate in dilute aqueous solutions affords dinuclear complexes of the [1+2]-condensation product (**1**) in yields up to 80%.[6] In aqueous-alcoholic solutions, the reaction with the use of the same reagent ratio gives complex **1** in lower yield (40%) and produces simultaneously dinuclear macrocyclic complexes **2**, which become the major reaction products in alcoholic solutions.



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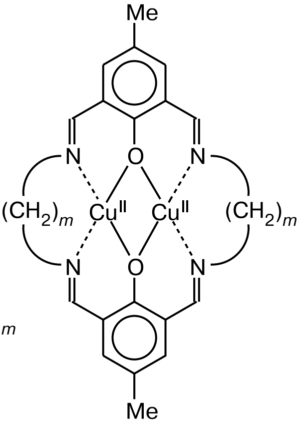

2

m = 3

Most of the known dinuclear copper(II) complexes are poorly soluble in nonpolar solvents, which constrains their use in the construction of homogeneous catalytic systems. In an effort to remedy this problem by introducing the *tert*-butyl group into the diformylphenol molecule and using trimethylacetate as an extra ligand, we studied

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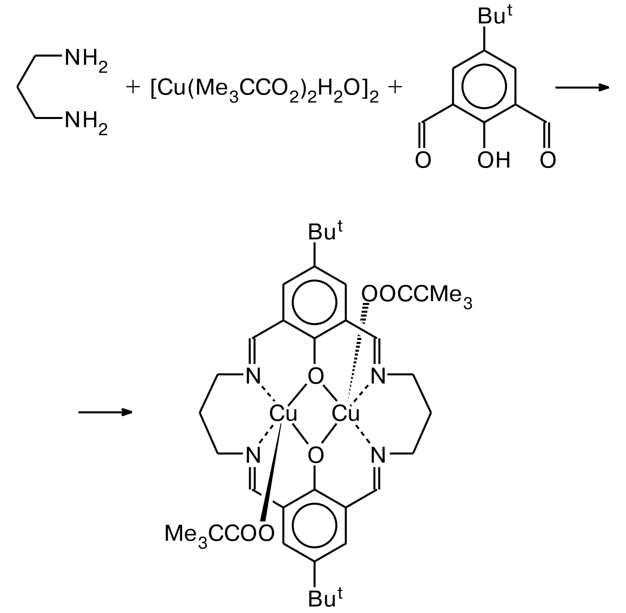
the reaction of 4-*tert*-butyl-2,6-diformylphenol with 1,3-diaminopropane in the presence of copper(II) trimethylacetate. It appeared that a new dinuclear copper(II) complex (**3**) with the macrocyclic Schiff base as a ligand was formed as the only product regardless of the reagent ratio, which was varied from 1 : 1 to 1 : 4, and the solvent (alcohol and aqueous-alcoholic mixtures were used). This stable pale-green crystalline compound is readily soluble in polar organic solvents and poorly soluble in water.



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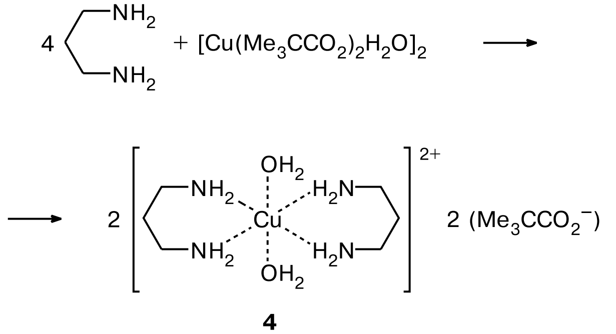
Attempts to use a large excess of diamine with the aim of preparing a complex of type **1** failed. These reactions gave the violet copper(II) complex with 1,3-diaminopropane (**4**) along with complex **3**.



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It was believed[7] that diamine, a dicarbonyl compound, or sometimes both starting reagents involved in template condensation form initially a complex with a metal ion followed by the formation of new azomethine bonds in the coordination sphere of the latter. It was demonstrated[8] that copper(II) complexes of dicarbonyl compounds give homodinuclear complexes with macrocyclic Schiff bases upon treatment with diamine. We found that complex **4** can also serve as an intermediate in template condensation. The reaction of complex **4** with 4-*tert*-butyl-2,6-diformylphenol afforded complex **3** in 62% yield.

Complex **3** was prepared as green crystals readily soluble in water, ethanol, and dioxane. It was characterized by X-ray diffraction analysis, mass spectrometry,

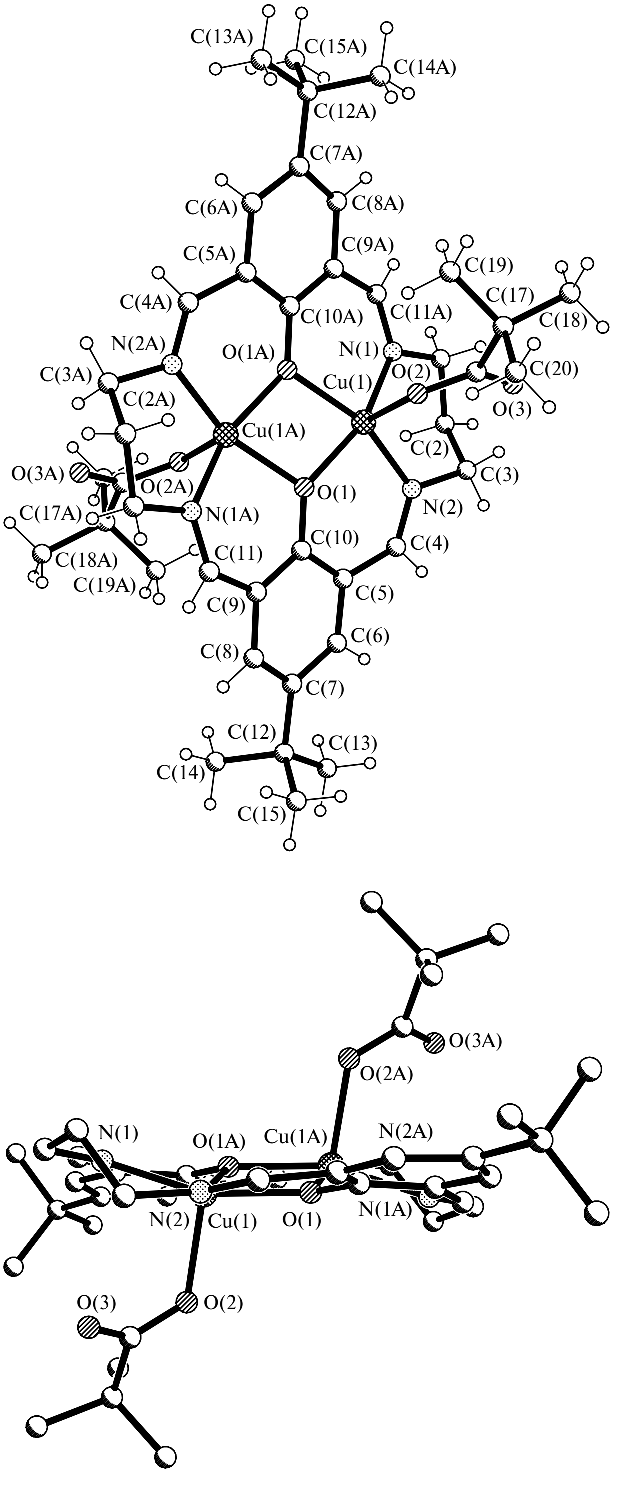


Fig. 1. Structure of dinuclear complex **3** in two projections.

Table 1. Bond lengths (d) and bond angles (ω) in complex **3**

Bond	d/Å	Bond	d/Å	Angle	ω/deg	Angle	ω/deg
Cu(1)—N(2)	1.961(2)	C(5)—C(6)	1.404(3)	N(2)—Cu(1)—O(1)	91.42(8)	C(4)—N(2)—C(3)	115.3(2)
Cu(1)—O(1)	1.9844(19)	C(5)—C(10)	1.406(4)	N(2)—Cu(1)—N(1)	96.86(9)	C(4)—N(2)—Cu(1)	125.93(18)
Cu(1)—N(1)	1.986(2)	C(6)—C(7)	1.379(4)	O(1)—Cu(1)—N(1)	159.65(8)	C(3)—N(2)—Cu(1)	118.42(16)
Cu(1)—O(1)$^{\#1}$	2.0072(19)	C(7)—C(8)	1.388(4)	N(2)—Cu(1)—O(1)$^{\#1}$	159.51(8)	N(1)—C(1)—C(2)	113.0(2)
Cu(1)—O(2)	2.151(2)	C(7)—C(12)	1.530(3)	O(1)—Cu(1)—O(1)$^{\#1}$	75.74(8)	C(3)—C(2)—C(1)	112.1(2)
O(1)—C(10)	1.325(3)	C(8)—C(9)	1.397(3)	N(1)—Cu(1)—O(1)$^{\#1}$	90.72(8)	N(2)—C(3)—C(2)	108.1(2)
O(1)—Cu(1)$^{\#1}$	2.0072(19)	C(9)—C(10)	1.404(4)	N(2)—Cu(1)—O(2)	107.88(9)	N(2)—C(4)—C(5)	126.8(2)
O(2)—C(16)	1.268(3)	C(9)—C(11)	1.459(4)	O(1)—Cu(1)—O(2)	98.76(8)	O(1)—C(10)—C(9)	120.7(2)
O(3)—C(16)	1.233(4)	C(11)—N(1)$^{\#1}$	1.276(3)	N(1)—Cu(1)—O(2)	96.33(8)	O(1)—C(10)—C(5)	122.2(2)
N(1)—C(11)$^{\#1}$	1.276(3)	C(12)—C(13)	1.507(4)	O(1)$^{\#1}$—Cu(1)—O(2)	90.06(8)	C(9)—C(10)—C(5)	117.0(2)
N(1)—C(1)	1.481(3)	C(12)—C(15)	1.515(5)	C(10)—O(1)—Cu(1)	128.25(17)	O(3)—C(16)—O(2)	125.6(3)
N(2)—C(4)	1.277(3)	C(12)—C(14)	1.542(4)	Cu(1)—O(1)—Cu(1)$^{\#1}$	104.26(8)	O(3)—C(16)—C(17)	118.7(2)
N(2)—C(3)	1.475(3)	C(16)—C(17)	1.551(4)	C(16)—O(2)—Cu(1)	120.97(18)	O(2)—C(16)—C(17)	115.7(2)
C(1)—C(2)	1.517(3)	C(17)—C(18)	1.522(4)	C(11)$^{\#1}$—N(1)—C(1)	113.4(2)	C(18)—C(17)—C(16)	110.8(2)
C(2)—C(3)	1.505(3)	C(17)—C(20)	1.524(4)	C(11)$^{\#1}$—N(1)—Cu(1)	122.23(18)	C(20)—C(17)—C(16)	107.8(2)
C(4)—C(5)	1.444(4)	C(17)—C(19)	1.531(4)	C(1)—N(1)—Cu(1)	123.75(16)	C(19)—C(17)—C(16)	109.6(2)

IR spectroscopy, and elemental analysis. Two projections of the molecular structure of complex **3** are shown in Fig. 1. Selected geometric parameters are given in Table 1. Crystallographic characteristics are listed in Table 2. In the cavity of the macrocyclic ligand, two copper atoms are bound to two bridging oxygen atoms of the phenol groups of the macrocycle and are located at a distance of 3.151(1) Å from each other. The tetragonal-pyramidal coordination of the copper atoms also involves the nitrogen atoms of the macrocycle and the oxygen atoms of the trimethylacetate anions, which are in the mutual *trans* positions with respect to the mean plane of the

Table 2. Crystallographic data and details of X-ray diffraction study for complexes **3**, **4**, **5a**, **5b**, and **7**

Parameter	**3**	**4**	**5a**	**5b**	**7**
Molecular formula	$C_{40}H_{56}Cu_2N_4O_6$	$C_{16}H_{42}CuN_4O_6$	$C_{34}H_{42}Cl_{14}Cu_2N_4O_2$	$C_{34}H_{42}Cl_{14}Cu_2N_4O_2$	$C_{52}H_{64}Cl_6Cu_2N_4O_8$
Space group	$P\bar{1}$	$P\bar{1}$	$P2_1/n$	$P2_1/c$	$P2(1)/n$
Unit cell parameters:					
a/Å	6.533(2)	6.763(12)	6.893(2)	6.767(5)	16.22(4)
b/Å	10.104(4)	6.940(11)	17.368(5)	19.91(2)	9.98(3)
c/Å	14.557(5)	12.354(15)	20.351(6)	17.732(13)	18.27(4)
α/deg	91.901(7)	77.92(4)	90	90	90
β/deg	90.493(7)	84.48(6)	97.714(7)	93.60(2)	108.46(13)
γ/deg	91.885(8)	83.41(7)	90	90	90
V/Å^3	959.8(6)	561.7(15)	2414.2(12)	2385(3)	2804(12)
Z		1	1	2	2 2
ρ_{calc}/g cm^{-3}	1.412	1.330	1.599	1.618	1.436
Absorption coefficient/cm^{-1}	1.159	1.008	1.691	1.712	1.099
θ scan range/deg	2.02—30.11	3.04—29.99	2.02—30.01	1.54—30.03	1.47—30.41
Indices of reflections	$-9 \le h \le 9$, $-14 \le k \le 11$, $-20 \le l \le 20$	$-6 \le h \le 9$, $-9 \le k \le 4$, $-17 \le l \le 11$	$-7 \le h \le 9$, $-24 \le k \le 22$, $-14 \le l \le 28$	$-5 \le h \le 9$, $-28 \le k \le 27$, $-16 \le l \le 24$	$-11 \le h \le 22$, $-13 \le k \le 8$, $-25 \le l \le 24$
Number of independent reflections	5050 (R_{int} = 0.0280)	2542 (R_{int} = 0.0233)	4294 (R_{int} = 0.0340)	5360 (R_{int} = 0.0785)	5617 (R_{int} = 0.0538)
GOOF based on F^2	1.000	0.903	1.010	0.998	1.009
R ($I > 2\sigma(I)$)					
R_1	0.0504	0.0581	0.0660	0.0630	0.0784
wR_2	0.1316	0.1541	0.1305	0.1449	0.1785
R (all reflections)					
R_1	0.0593	0.0607	0.0919	0.0753	0.1030
wR_2	0.1371	0.1586	0.1361	0.1550	0.1905

macrocycle. The copper atoms deviate by 0.299 Å from the corresponding N_2O_2 planes of the bases of the pyramids toward the apical oxygen atoms. The polydentate coordination of the macrocyclic ligand in complex **3** results in the formation of seven metallocycles, *viz.*, one planar four-membered $\{Cu_2O_2\}$ ring and six six-membered rings. The six-membered {Cu(1)O(1)C(4)C(5)C(10)N(2)} and {Cu(1a)O(1a)C(4a)C(5a)C(10a)N(2a)} metallocycles related to each other by a crystallographic center of symmetry are planar. Two other metallocycles, *viz.*, {Cu(1)N(1)C(1)C(2)C(3)N(2)} and {Cu(1a)N(1a)C(1a)C(2a)C(3a)N(2a)}, adopt a half-boat conformation with the C(1) and C(2) atoms deviating in the same direction from the plane through the other four atoms by 0.18 and 0.78 Å, respectively. The {Cu(1)N(2)C(4)C(5)C(6)O(1)} and {Cu(1a)N(2a)C(4a)C(5a)C(6a)O(1a)} metallocycles also adopt a half-boat conformation with the Cu(1) and N(2) atoms deviating in the same direction from the plane through the other four atoms by 0.88 and 0.29 Å, respectively.

In the IR spectrum of complex **3**, the stretching vibration band of the C=N group (1634 and 1644 cm^{-1}) and the stretching vibration band of the carboxylate ligands (1566 and 1577 cm^{-1}) are split. The splitting of these bands is retained in going from the crystalline state to a solution in dioxane.

The structure of complex **4** established by X-ray diffraction analysis (Fig. 2) consists of the centrosymmetrical complex cations $[Cu(C_3H_{10}N_2)_2 \cdot 2H_2O]^{2+}$ and the trimethylacetate anions $[(OOCBu^t)]^-$. In the crystal, the cations and anions are linked by hydrogen bonds. Selected geometric parameters of molecule **4** are given in Table 3. Crystallographic characteristics are listed in Table 2. The copper(II) atom is in a distorted tetragonal-bipyramidal environment formed by four nitrogen atoms of two chelate propylenediamine ligands (Cu—N, 2.026 and 2.032(3) Å) in the base of the pyramid and two water molecules in the axial positions (Cu—O(w1), 2.618(3) Å). The six-membered metallocycle adopts a chair conformation typical of such rings.

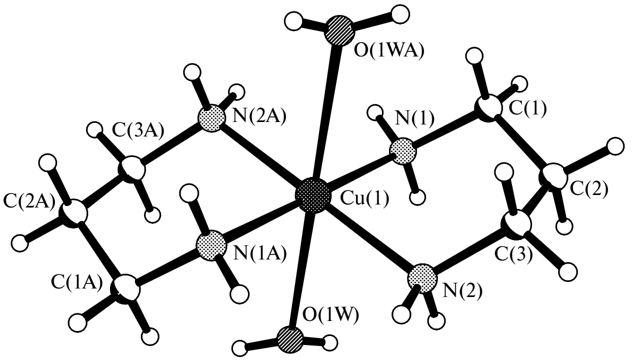


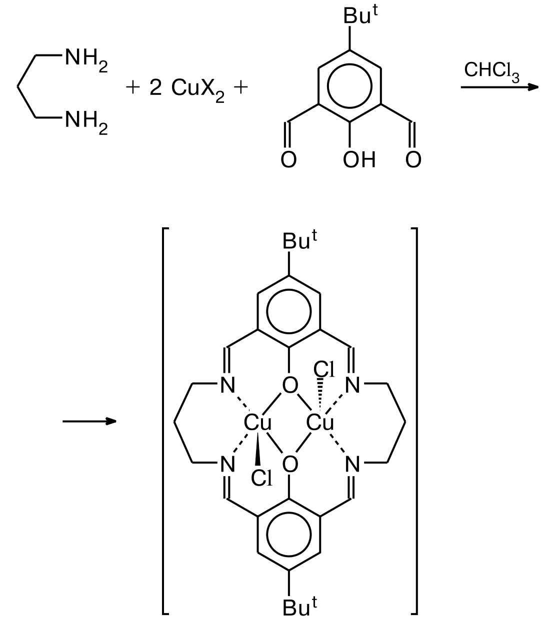
Fig. 2. Molecular structure of the cation of complex **4**.

Table 3. Bond lengths (*d*) and bond angles (ω) in complex **4**

Bond	*d*/Å	Angle	ω/deg
Cu(1)—N(1)$^{\#1}$	2.026(3)	N(1)$^{\#1}$—Cu(1)—N(1)	180.0
Cu(1)—N(1)	2.026(3)	N(1)$^{\#1}$—Cu(1)—N(2)$^{\#1}$	87.76(11)
Cu(1)—N(2)$^{\#1}$	2.032(3)	N(1)—Cu(1)—N(2)$^{\#1}$	92.24(11)
Cu(1)—N(2)	2.032(3)	N(1)$^{\#1}$—Cu(1)—N(2)	92.24(11)
O(1)—C(4)	1.265(3)	N(1)—Cu(1)—N(2)	87.76(11)
O(2)—C(4)	1.256(3)	N(2)$^{\#1}$—Cu(1)—N(2)	180.0
N(1)—C(1)	1.495(4)	C(1)—N(1)—Cu(1)	113.33(17)
N(2)—C(3)	1.488(4)	C(3)—N(2)—Cu(1)	115.57(18)
C(1)—C(2)	1.517(4)	N(1)—C(1)—C(2)	111.9(2)
C(2)—C(3)	1.526(4)	C(1)—C(2)—C(3)	115.5(2)
C(4)—C(5)	1.547(4)	N(2)—C(3)—C(2)	110.9(2)
C(5)—C(8)	1.531(4)	O(2)—C(4)—O(1)	123.6(2)
C(5)—C(7)	1.532(4)	O(2)—C(4)—C(5)	119.1(2)
C(5)—C(6)	1.534(4)	O(1)—C(4)—C(5)	117.3(2)
		C(8)—C(5)—C(7)	109.4(2)
		C(8)—C(5)—C(6)	109.4(2)
		C(7)—C(5)—C(6)	109.2(2)
		C(8)—C(5)—C(4)	108.0(2)
		C(7)—C(5)—C(4)	108.9(2)
		C(6)—C(5)—C(4)	111.9(2)

In the IR spectrum of complex **4**, the stretching vibration band of the carboxylate group is unsplit (1545 cm^{-1}), the N—H stretching vibrations are observed as a set of bands at 3146, 3243 and 3296 cm^{-1} in the region of O—H stretching vibrations of the H_2O molecules manifested as a broad band at 3444 cm^{-1}, and the N—H bending band is observed at 1647 cm^{-1}.

Storage of a solution of complex **3** in chloroform over a long period leads to exchange of the trimethylacetate



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X = AcO, Cl

Table 4. Bond lengths (*d*) and bond angles (ω) in complexes **5a** and **5b**

Parameter	**5a**	**5b**	Parameter	**5a**	**5b**	Parameter	**5a**	**5b**
Bond	*d*/Å		Angle	ω/deg		Angle	ω/deg	
Cu(1)—N(1)	1.971(4)	1.954(3)	N(1)—Cu(1)—N(2)	96.43(17)	97.01(13)	N(2)—C(4)—C(5)	128.0(5)	128.4(3)
Cu(1)—N(2)	1.980(4)	1.981(3)	N(1)—Cu(1)—O(1)	163.13(16)	163.49(12)	C(11)—C(5)—C(4)	115.4(5)	115.8(3)
Cu(1)—O(1)	1.988(3)	1.975(3)	N(2)—Cu(1)—O(1)	91.82(15)	91.81(12)	C(11)—C(5)—C(6)	119.7(5)	120.0(3)
Cu(1)—O(1)$^{\#1}$	1.992(3)	1.989(3)	N(1)—Cu(1)—O(1)$^{\#1}$	91.91(15)	91.70(12)	C(6)—C(5)—C(4)	124.9(5)	124.2(3)
Cu(1)—Cl(1)	2.5168(15)	2.4899(16)	N(2)—Cu(1)—O(1)$^{\#1}$	162.14(15)	163.58(12)	O(1)—C(6)—C(5)	120.4(5)	120.8(3)
O(1)—C(6)	1.324(6)	1.332(4)	O(1)—Cu(1)—O(1)$^{\#1}$	76.38(14)	76.58(11)	O(1)—C(6)—C(7)	122.4(5)	121.8(3)
O(1)—Cu(1)$^{\#1}$	1.992(3)	1.989(3)	N(1)—Cu(1)—Cl(1)	96.23(13)	98.94(11)	C(7)—C(6)—C(5)	117.1(5)	117.3(3)
N(1)—C(8)$^{\#1}$	1.284(6)	1.283(5)	N(2)—Cu(1)—Cl(1)	94.73(13)	93.86(10)	C(6)—C(7)—C(8)	123.6(5)	124.3(3)
N(1)—C(1)	1.452(6)	1.480(5)	O(1)—Cu(1)—Cl(1)	97.72(11)	94.33(10)	C(6)—C(7)—C(9)	120.7(5)	119.8(3)
N(2)—C(3)	1.486(7)	1.488(5)	O(1)$^{\#1}$—Cu(1)—Cl(1)	100.05(11)	98.52(9)	C(9)—C(7)—C(8)	115.6(5)	115.9(3)
N(2)—C(4)	1.293(7)	1.278(5)	C(6)—O(1)—Cu(1)	125.7(3)	124.9(2)	N(1)$^{\#1}$—C(8)—C(7)	129.2(5)	127.4(3)
C(1)—C(2)	1.525(7)	1.511(5)	C(6)—O(1)—Cu(1)$^{\#1}$	128.4(3)	128.2(2)	C(10)—C(9)—C(7)	122.5(5)	123.6(4)
C(2)—C(3)	1.511(8)	1.509(5)	Cu(1)—O(1)—Cu(1)$^{\#1}$	103.62(14)	103.42(11)	C(9)—C(10)—C(12)	122.3(5)	122.5(3)
C(4)—C(5)	1.435(8)	1.440(5)	C(8)$^{\#1}$—N(1)—C(1)	117.2(4)	115.7(3)	C(11)—C(10)—C(9)	116.0(5)	115.4(3)
C(5)—C(6)	1.418(7)	1.416(5)	C(8)$^{\#1}$—N(1)—Cu(1)	123.9(4)	125.6(3)	C(11)—C(10)—C(12)	121.6(5)	122.0(3)
C(5)—C(11)	1.416(7)	1.402(5)	C(1)—N(1)—Cu(1)	118.9(3)	118.7(2)	C(10)—C(11)—C(5)	123.5(5)	123.6(3)
C(6)—C(7)	1.401(7)	1.410(5)	C(4)—N(2)—C(3)	112.7(4)	113.0(3)	C(10)—C(12)—C(14)	113.0(5)	112.2(3)
C(7)—C(8)	1.436(7)	1.440(5)	C(3)—N(2)—Cu(1)	124.3(3)	124.0(2)	C(10)—C(12)—C(15)	108.9(5)	110.1(3)
C(7)—C(9)	1.414(7)	1.413(5)	C(4)—N(2)—Cu(1)	122.1(4)	121.8(3)	C(13)—C(12)—C(10)	110.3(6)	108.8(3)
C(8)—N(1)$^{\#1}$	1.284(6)	1.283(5)	N(1)—C(1)—C(2)	110.7(4)	110.1(3)	C(13)—C(12)—C(14)	109.5(6)	109.4(4)
C(9)—C(10)	1.393(7)	1.385(5)	C(3)—C(2)—C(1)	111.6(5)	112.5(3)	C(13)—C(12)—C(15)	109.8(6)	108.0(3)
C(10)—C(11)	1.377(8)	1.393(5)	N(2)—C(3)—C(2)	113.2(4)	114.3(3)	C(14)—C(12)—C(15)	105.3(6)	108.3(3)
C(10)—C(12)	1.522(7)	1.534(5)						
C(12)—C(13)	1.474(9)	1.515(6)						
C(12)—C(14)	1.546(10)	1.542(6)						
C(12)—C(15)	1.541(9)	1.531(6)						

anions with the chloride ions to form complex **5a**, which crystallizes with four chloroform molecules. The synthesis of complex **3** with the use of Cu^{II} acetate instead of copper(II) trimethylacetate followed by storage in chloroform afforded chloride complex **5b**, which also crystallized with four solvent molecules but in a different polymorphous modification. Complex **5b** was also prepared by condensation of 4-*tert*-butyl-2,6-diformylphenol with 1,3-diaminopropane in the presence of copper(II) chloride. Both complexes crystallize as large dark-green crystals readily soluble in polar organic solvents and water.

In the IR spectra of complexes **5a** and **5b**, the C=N stretching vibration band is observed at 1639 cm^{-1} and is unsplit.

Selected crystallographic parameters of complexes **5a** and **5b** are given in Table 2. Main bond lengths and bond angles are listed in Table 4. The structures of complexes

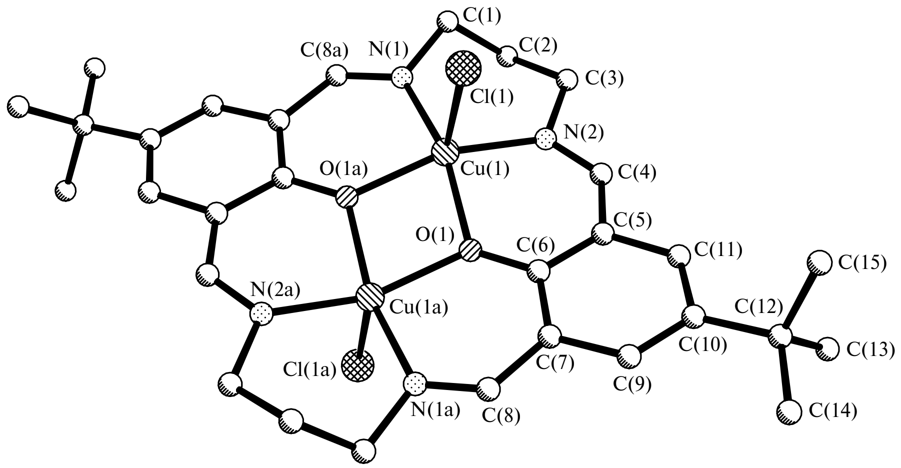
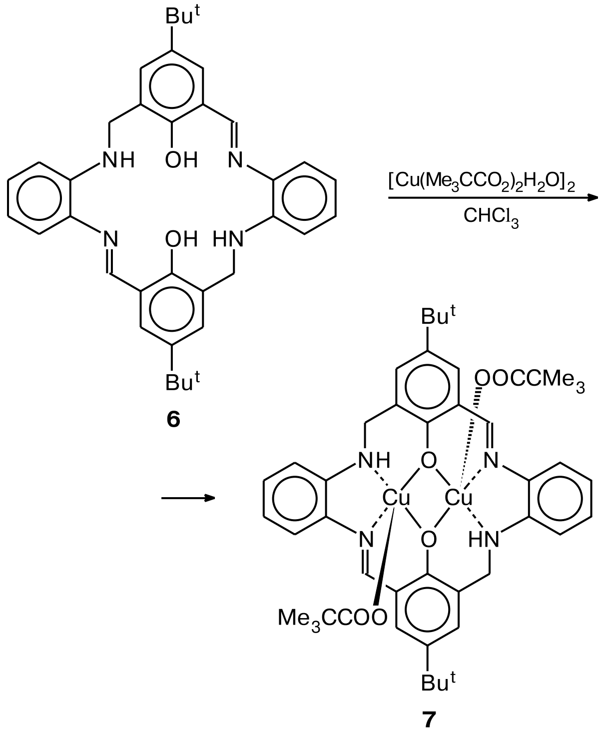


Fig. 3. Molecular structure of complex **5**.

5a and **5b** are virtually identical (Fig. 3) and are as a whole similar to the structure of complex **3**. The polymorphous modifications of compounds **5a** and **5b** differ only in the positions of the chloroform solvate molecules. In both structures, these molecules are disordered. Two of three chlorine atoms in the solvate molecules occupy two positions each with approximately 50% occupancies and differ in the angle of rotation with respect to the bond between the carbon and chlorine atoms (occupancies of their positions are 100%).

In the cavity of the ligand, two copper atoms are bound to two bridging oxygen atoms of the phenol groups of the macrocycle. The Cu...Cu distances are 3.128(1) and 3.111(1) Å in molecules **5a** and **5b**, respectively. The tetragonal-pyramidal coordination of the copper(II) atoms involves also the N atoms of the macrocycle and the terminal Cl atoms in the mutual *trans* positions with respect to the mean plane of the macrocycle. The deviations of the copper atoms from the corresponding N_2O_2 planes in the bases of the pyramid toward the apical chloride ligands are 0.243 and 0.221 Å in molecules **5a** and **5b**, respectively, compared to 0.229 Å in complex **3**. As in complex **3**, the four-membered {Cu_2O_2} metallocycles in complexes **5** are planar and the six-membered {Cu(1a)O(1)C(6)C(7)C(8)N(1a)} and {Cu(1)O(1a)C(6a)C(7a)C(8a)N(1)} metallocycles are nearly planar. In the latter metallocycles, the C(7) atom is characterized by the maximum deviation from the mean plane (0.045 and 0.065 Å in molecules **5a** and **5b**, respectively). As in complex **3**, the remaining four six-membered metallocycles in molecules **5a** and **5b** are nonplanar. However, two of them, *viz.*, {Cu(1)N(1)C(1)C(2)C(3)N(2)} and {Cu(1a)N(1a)C(1a)C(2a)C(3a)N(2a)}, in molecules **5** adopt a half-chair conformation (half-boat in molecule **3**) with the C(1) and C(2) atoms deviating in opposite directions from the plane through the other four atoms by 0.346 and 0.485 Å (in molecule **5a**), 0.388 and 0.443 Å (in molecule **5b**), respectively. Two other metallocycles, *viz.*, {Cu(1)N(2)C(4)C(5)C(6)O(1)} and {Cu(1a)N(2a)C(4a)C(5a)C(6a)O(1a)}, in complexes **5**,



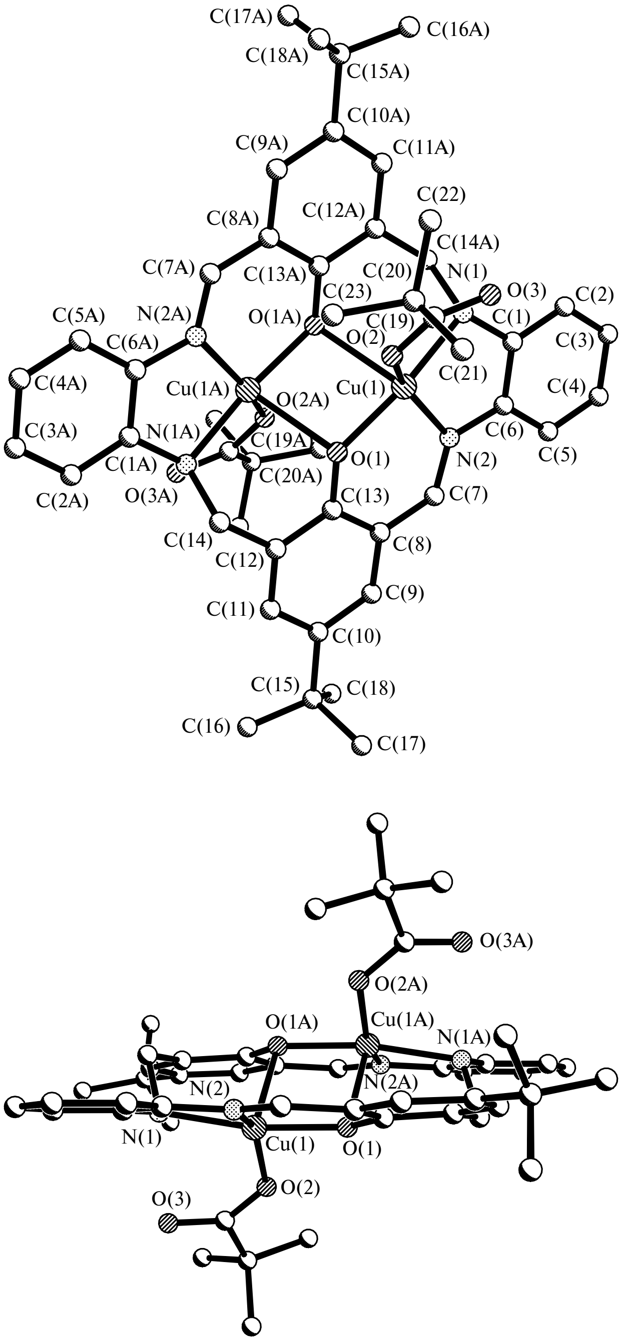


Fig. 4. Molecular structure of complex **7** in two projections.

like those in complex **3**, adopt a half-boat conformation. The Cu(1) and N(2) atoms in these metallocycles deviate in the same direction from the planes through the other four atoms (by 0.665 and 0.199 Å in molecule **5a**, by 0.687 and 0.176 Å in molecule **5b**).

Earlier, we have prepared partially reduced macrocyclic Schiff base **6** by the reaction of 2,6-diformyl-4-*tert*-butylphenol with 1,2-diaminobenzene.[9] The reaction of compound **6** with copper(II) trimethylacetate in chloroform afforded the dinuclear copper complex (**7**) as large green crystals in virtually quantitative yield. The crystals are soluble only in polar organic solvents.

The structure of complex **7** was established by X-ray diffraction analysis (Fig. 4). Selected geometric parameters of complex **7** are given in Table 5. Crystallographic characteristics are listed in Table 2.

As in complexes **3** and **5**, two copper atoms in molecule **7** are located in the cavity of the macrocyclic ligand at a distance of 3.159(1) Å from each other and are bound to two bridging oxygen atoms of the phenol groups of the macrocycle. The tetragonal-pyramidal coordination of the copper atoms in molecule **7** is distorted to an extent that it can be considered as a trigonal-bipyramidal coordination with the N(1) and O(1) atoms (N—Cu—O, 170.0°) in the apical positions and the O(1a) O(2), and N(2) atoms in the equatorial plane. Correspondingly, the apical Cu—O(1) bond length (1.896 Å) is substantially smaller than the equatorial Cu—O(1a) bond length (2.278 Å). The trimethylacetate groups are in the mutual *trans* positions with respect to the plane of the central Cu_2O_2 fragment. The four-membered Cu_2O_2 metallocycle, the six-membered {Cu(1)O(1)C(7)C(8)C(13)N(2)} and {Cu(1a)O(1a)C(4a)C(5a)C(10a)N(2a)} metallocycles, and the five-membered {Cu(1)N(1)N(2)C(1)C(6)} and {Cu(1a)N(1a)N(2a)C(1a)C(6a)} metallocycles are planar. Two other six-membered {Cu(1)O(1a)C(13a)C(12a)C(14a)N(1)} and {Cu(1a)O(1)C(13)C(12)C(14)N(1a)} metallocycles are folded along the N(1)...C(13a) and N(1a)...C(13) lines and adopt a half-boat conformation with the Cu(1) and N(1) atoms deviating from the planes through the other four atoms in the same direction by 1.80 and 1.30 Å, respectively. As a result of substantial deviation of these two metallocycles from planarity, complex **7** has a "staircase"-like structure. Formally, three planar fragments, *viz.*, the central Cu_2O_2 group and two halves of the macrocycle,

Table 5. Bond lengths (*d*) and bond angles (ω) in complex **7**

Bond	*d*/Å	Bond	*d*/Å	Angle	ω/deg	Angle	ω/deg
Cu(1)—O(1)	1.896(4)	C(9)—H(9A)	0.950(5)	O(1)—Cu(1)—O(2)	88.2(2)	N(2)—C(6)—C(5)	125.8(5)
Cu(1)—O(2)	1.955(4)	C(9)—C(10)	1.378(8)	O(1)—Cu(1)—N(1)	170.5(2)	C(1)—C(6)—C(5)	118.5(5)
Cu(1)—N(1)	1.995(5)	C(10)—C(11)	1.395(8)	O(1)—Cu(1)—N(2)	94.4(2)	N(2)—C(7)—H(7A)	116.8(5)
Cu(1)—N(2)	1.946(5)	C(10)—C(15)	1.542(9)	O(2)—Cu(1)—N(1)	96.7(2)	N(2)—C(7)—C(8)	126.3(5)
O(1)—C(13)	1.309(7)	C(11)—H(11A)	0.950(6)	O(2)—Cu(1)—N(2)	150.5(2)	H(7A)—C(7)—C(8)	116.8(5)
O(2)—C(19)	1.270(7)	C(11)—C(12)	1.375(8)	N(1)—Cu(1)—N(2)	85.3(2)	C(7)—C(8)—C(9)	117.0(5)
O(3)—C(19)	1.243(7)	C(12)—C(13)	1.394(8)	Cu(1)—O(1)—C(13)	127.7(3)	C(7)—C(8)—C(13)	124.2(5)
N(1)—C(1)	1.461(7)	C(12)—C(14)	1.510(8)	Cu(1)—O(2)—C(19)	126.8(4)	C(9)—C(8)—C(13)	118.7(5)
N(1)—C(14)	1.479(7)	C(15)—C(16)	1.48(1)	Cu(1)—N(1)—C(1)	107.7(3)	C(8)—C(9)—H(9A)	118.9(5)
N(2)—C(6)	1.409(7)	C(15)—C(17)	1.52(1)	Cu(1)—N(1)—C(14)	113.5(3)	C(8)—C(9)—C(10)	122.3(5)
N(2)—C(7)	1.291(7)	C(15)—C(18)	1.49(1)	C(1)—N(1)—C(14)	112.7(4)	H(9A)—C(9)—C(10)	118.8(5)
C(1)—C(2)	1.374(8)	C(16)—H(16A)	0.98(1)	Cu(1)—N(2)—C(6)	112.3(3)	C(9)—C(10)—C(11)	117.5(5)
C(1)—C(6)	1.388(8)	C(16)—H(16B)	0.98(1)	Cu(1)—N(2)—C(7)	124.0(4)	C(9)—C(10)—C(15)	121.2(5)
C(2)—H(2A)	0.950(6)	C(16)—H(16C)	0.98(1)	C(6)—N(2)—C(7)	123.5(5)	C(11)—C(10)—C(15)	121.0(5)
C(2)—C(3)	1.377(8)	C(17)—H(17A)	0.980(8)	N(1)—C(1)—C(2)	121.5(5)	C(10)—C(11)—H(11A)	119.0(6)
C(3)—H(3A)	0.950(6)	C(17)—H(17B)	0.980(8)	N(1)—C(1)—C(6)	117.4(5)	C(10)—C(11)—C(12)	122.0(5)
C(3)—C(4)	1.400(8)	C(17)—H(17C)	0.98(1)	C(2)—C(1)—C(6)	121.1(5)	H(11A)—C(11)—C(12)	119.0(6)
C(4)—H(4A)	0.950(6)	C(18)—H(18A)	0.980(7)	C(1)—C(2)—H(2A)	119.7(5)	C(11)—C(12)—C(13)	120.8(5)
C(4)—C(5)	1.374(8)	C(18)—H(18B)	0.980(9)	C(1)—C(2)—C(3)	120.6(5)	C(11)—C(12)—C(14)	120.8(5)
C(5)—H(5A)	0.950(6)	C(18)—H(18C)	0.980(8)	H(2A)—C(2)—C(3)	119.7(6)	C(13)—C(12)—C(14)	118.5(5)
C(5)—C(6)	1.389(8)	C(19)—C(20)	1.517(8)	C(2)—C(3)—H(3A)	120.7(6)	O(1)—C(13)—C(8)	123.0(5)
C(7)—H(7A)	0.950(6)	C(20)—C(21)	1.515(9)	C(2)—C(3)—C(4)	118.7(5)	O(1)—C(13)—C(12)	118.5(5)
C(7)—C(8)	1.421(8)	C(20)—C(22)	1.511(9)	H(3A)—C(3)—C(4)	120.7(6)	C(8)—C(13)—C(12)	118.5(5)
C(8)—C(9)	1.409(8)	C(20)—C(23)	1.527(8)	C(3)—C(4)—H(4A)	119.7(6)	N(1)—C(14)—C(12)	111.8(5)
C(8)—C(13)	1.418(8)			C(3)—C(4)—C(5)	120.6(5)	C(10)—C(15)—C(16)	112.0(7)
				H(4A)—C(4)—C(5)	119.7(6)	C(10)—C(15)—C(17)	108.7(6)
				C(4)—C(5)—H(5A)	119.8(6)	C(10)—C(15)—C(18)	110.1(6)
				C(4)—C(5)—C(6)	120.5(5)	C(16)—C(15)—C(17)	109.1(7)
				H(5A)—C(5)—C(6)	119.8(6)	C(16)—C(15)—C(18)	111.3(7)
				N(2)—C(6)—C(1)	115.7(5)	C(17)—C(15)—C(18)	105.3(6)

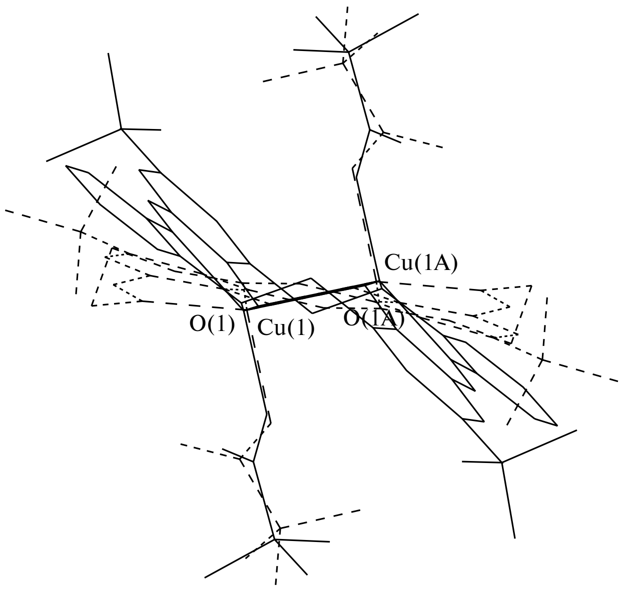


Fig. 5. Superposition of the structures of complexes **3** (dashed lines) and **7** (solid lines).

are present in the complex. The angle between the plane passing through the atoms of the central ring and the plane formed by the coplanar N(1), N(2), O(1), and C(8)—C(13) atoms is 124.2°. The analogous folding angles in the structures of **3** and **5** are 158.4° and 165.4°, respectively. A superposition of complexes **3** and **7** (central Cu_2O_2 fragments of both structures completely coincide with each other) is shown in Fig. 5.

In the crystal, molecules **7** are linked to the ethanol and chloroform solvate molecules through hydrogen bonds and van der Waals interactions. The ethanol solvate molecule is linked to the O(3) atom of the trimethylacetate group of the complex by the intermolecular O—H...O(3) hydrogen bond (H...O, 1.84 Å; O...O, 2.681 Å; O—H...O, 176°). The crystal packing of **7** is shown in Fig. 6.

A comparison of the geometric parameters of dinuclear complexes **3**, **5**, and **7** clearly shows their structural similarity.

Quantum-chemical study of dinuclear complexes **3** and **5** by the density functional theory (gradient-cor-

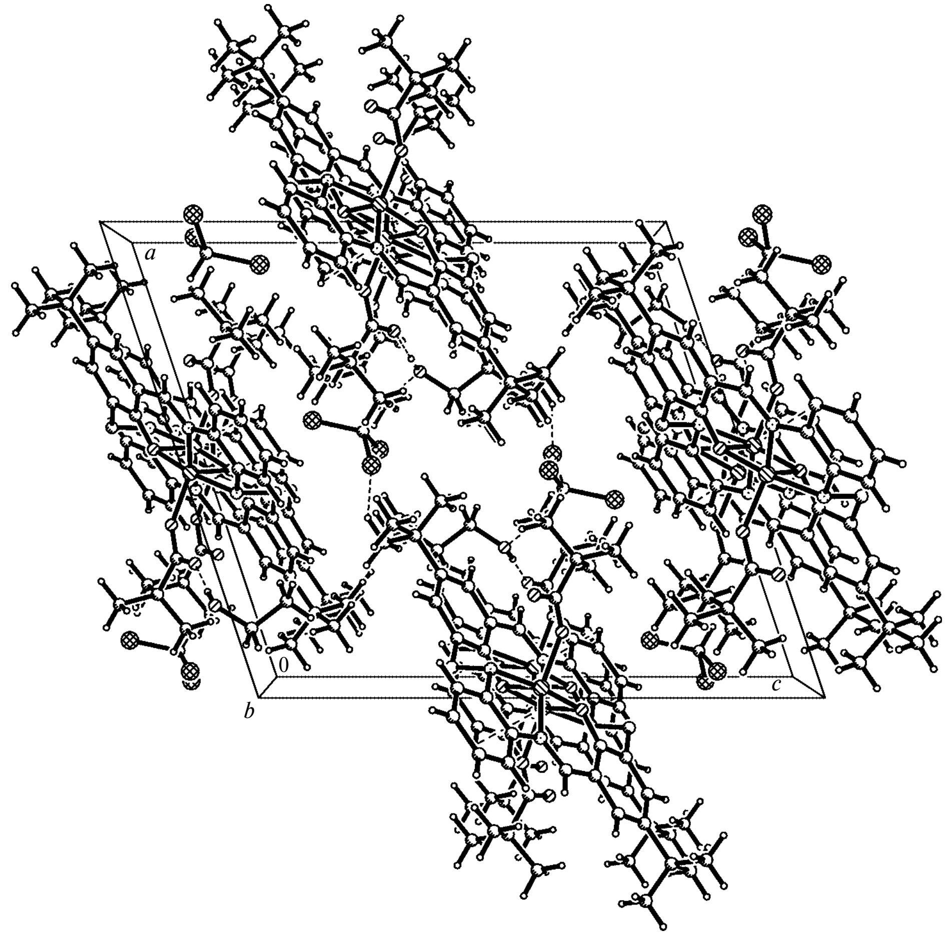


Fig. 6. Crystal packing of complex **7**.

rected PBE functional, the TZ2p basis set) revealed minima on their potential energy surfaces corresponding to triplet and singlet states. The energies of the triplet states are lower than those of the singlet states by 2.08 and 5.74 kcal mol^{-1} for molecules **3** and **5**, respectively. On the whole, the geometric parameters of the triplet complexes are similar to those determined by X-ray diffraction analysis. According to the results of calculations, the isolated molecules of complexes **3** and **5** have a centrosymmetrical structure with the metal atoms in a tetragonal-pyramidal environment formed by the oxygen and nitrogen atoms of the macrocycle in the basal plane and the chlorine or oxygen atom of the trimethylacetate ligand in the apical position. In complexes **3** and **5**, the calculated Cu...Cu distances are 3.08 and 3.44 Å, respectively. According to the results of calculations, the copper atoms deviate from the basal planes of the macrocycles, which is consistent with the results of X-ray diffraction analysis. However, these deviations (0.163 Å for complex **3** and 0.426 Å for complex **5**) are somewhat underestimated compared to the experimental values.

For molecule **7**, the calculated minimum corresponding to the triplet complex is 6.19 kcal mol^{-1} higher than the minimum for the singlet complex. Nevertheless, the geometric parameters of the triplet complex are also in much better agreement with the results of X-ray diffraction analysis. The distance between the metal atoms in the centrosymmetrical complex is 3.429 Å. The metal atoms deviate from the basal planes by 0.956 Å. The macrocyclic ligand adopts a staircase conformation. The angle between the planes of the phenol and *o*-phenylenediamine rings is 140°, which is consistent with the experimental data.

We failed to measure well-resolved ^{1}H and ^{13}C NMR spectra of dinuclear complexes **3**, **5**, and **7**. As expected, all signals in these spectra are paramagnetically broadened.

To summarize, we synthesized three new dinuclear Cu^{II} complexes and established their structures by X-ray diffraction analysis. All these complexes have a centrosymmetrical structure with the copper atoms in a tetragonal-pyramidal coordination and are of interest as models of active centers of copper-containing proteins. In all complexes, the metal atoms deviate substantially from the basal plane toward the apical ligand.

Experimental

X-ray diffraction data for complexes **3**, **4**, **5a**, **5b**, and **7** were collected according to a standard procedure[10] on a Bruker AXS SMART 1000 diffractometer equipped with a CCD detector (λMo, graphite monochromator, 110 K, ω scanning technique, scan step was 0.3°, frames were exposed for 30 s, $2\theta_{max} = 60°$). The semiempirical absorption corrections were applied.[11] The structures were solved by direct methods using the SHELXS97 program package[12] and refined by the full-matrix least-squares method with anisotropic thermal parameters (positions of hydrogen atoms were kept fixed with $U_H = 0.08$ Å^2) using the SHELXL97 program package.[13] The IR spectra were recorded on a Specord M80 (in KBr pellets) and UR-2 (in Nujol mulls) spectrometers. The chemical-ionization positive ion mass spectra were measured on a MALDI-TOF Reflex 3 Bruker instrument equipped with an UV laser (337 nm).

Theoretical investigation. Potential energy surfaces were studied by the density functional theory using the original PRIRODA program created by Laikov.[14] The PBE functional, which involves the electron density gradient,[15] was used. The Kohn—Sham equations were solved using the TZ2p atomic basis sets of the grouped Gaussian functions. The orbital basis sets included the contraction sets (5s1p)/[3s1p] for H and (11s6p2d)/[6s3p2d] for C, N, and O. The matrix elements of the Coulomb and exchange-correlation potentials were calculated using expansion of the electron density in an auxiliary basis set consisting of the atom-centered nongrouped Gaussian functions of the types (4*s*1*p*) for H and (3*s*2*d*1*f*) for C, N, and O.[14] The geometry was optimized without restrictions imposed on the molecular symmetry. The character of the stationary points was determined based on analytical calculations of the second derivatives of the energy. Earlier, this method and the PRIRODA program have been successfully used in the study of the structures and reactivities of silicon-containing organophosphorus betaines[16] and in examination of the mechanism of activation of alkanes with cationic titanium and zirconium complexes.[17]

Dichloro-11,23-(2,2-dimethylethyl)-25,26-dihyhdroxy-3,7,15,19-tetraazatricyclo[19.3.1.1^{9,13}]hexacosa-1(25),2,7,9,11,13(26),14,19,21,23-decadeceno-*N*,*N*′,*O*-dicopper(II) (5a). 1,3-Diaminopropane (0.21 mL, 2.52 mmol) was added to a suspension of copper(II) trimethylacetate (670 mg, 2.52 mmol) in methanol (50 mL). The reaction solution was added to a warm saturated solution of 4-*tert*-butyl-2,6-diformylphenol (519 mg, 2.52 mmol) in methanol (40 mL) and the mixture was refluxed for 3 h. Fractional crystallization with removal of the solvent afforded pale-green crystals of complex **3**. After recrystallization from water, complex **3** was obtained in a yield of 0.77 g (75%). Crystallization of **3** from chloroform on prolonged storage (up to 7 days) afforded crystals of **5a**. Complex **3**, t.decomp. 264—266 °C. Found (%): C, 58.79; H, 6.94; N, 6.81; Cu, 15.62. $C_{40}H_{56}Cu_2N_4O_6$. Calculated (%): C, 58.87; H, 6.92; N, 6.87; Cu, 15.57. IR (KBr), ν/cm^{-1}: 1634, 1644 (C=N); 1566, 1577 (COO$^-$). MS (MALDI-TOF), *m/z*: 612.1 $[LCu_2]^{2+}$, 550.2 $[LCu + 2 H]^{2+}$. Complex **5a**, t.decomp. >300 °C. Found (%): C, 41.89; H, 4.44; N, 6.32. $C_{30}H_{38}Cl_2Cu_2N_4O_2 \cdot 2CHCl_3$. Calculated (%): C, 41.62; H, 4.37; N, 6.07.

Bis(trimethylacetato)-11,23-(2,2-dimethylethyl)-25,26-dihyhdroxy-3,7,15,19-tetraazatricyclo[19.3.1.1^{9,13}]hexacosa-1(25),2,7,9,11,13(26),14,19,21,23-decadeceno-*N*,*N*′,*O*-dicopper(II) (3) and diaqua-bis(trimethylacetato)bis(μ$_2$-1,3-propylenediaminato-*N*,*N*′)copper(II) (4). A solution of copper(II) trimethylacetate (1.29 g, 4.85 mmol) and 1,3-diaminopropane (0.81 mL, 9.70 mmol) in ethanol (69 mL) and water (10 mL) was added to a warm solution of 4-*tert*-butyl-2,6-diformylphenol (0.5 g, 2.43 mmol) and NaOH (0.097 g, 2.43 mmol) in water (300 mL) and ethanol (100 mL). The solution was concentrated to 10 mL under atmospheric pressure and then a 20-fold (by volume) excess of 1,4-dioxane was added. The precipitate of complex **4** that formed was filtered off. After recrystallization from a 1 : 10 methanol—tetrahydrofuran mixture, complex **4** was obtained in a yield of 435 mg (20%). The mother liquor was concentrated to prepare complex **3** in a yield of 357 mg (18%). Complex **4**, t.decomp. 203—205 °C. Found (%): C, 45.46; H, 9.38; N, 13.26; Cu, 15.48. $C_{16}H_{38}CuN_4O_4 \cdot 0.5H_2O$. Calculated (%): C, 45.43; H, 9.29; N, 13.24; Cu, 15.02. IR (KBr), ν/cm^{-1}: 1545 (COO^-); 3146, 3243, 3296 (N—H); 1647 (N—H).

Synthesis of complex 3. Complex **4** (677 mg, 0.97 mmol) and 4-*tert*-butyl-2,6-diformylphenol (199 mg, 0.97 mmol) were successively dissolved with stirring in anhydrous methanol (6 mL). The reaction mixture was stirred at ~20 °C for 12 h. The course of the reaction was monitored by TLC on Silufol (CH_2Cl_2 as the eluent). The solution was concentrated *in vacuo* to 0.25 of the initial volume. Dark-green crystals of complex **3** slowly precipitated from the methanolic solution upon prolonged storage under an atmosphere of diethyl ether. The crystals were filtered off and dried in air. Complex **3** was obtained in a yield of 245 mg (62%).

Dichloro-11,23-(2,2-dimethylethyl)-25,26-dihyhdroxy-3,7,15,19-tetraazatricyclo[19.3.1.1^{9,13}]hexacosa-1(25),2,7,9,11,13(26),14,19,21,23-decadeceno-*N*,*N*´,*O*-dicopper(II) (5b). ***A.*** A mixture of copper(II) acetate crystal hydrate (2.5 g, 12.5 mmol) and 1,3-diaminopropane (1.26 mL) in water (25 mL) was added to a warm solution of 4-*tert*-butyl-2,6-diformylphenol (0.91 g, 5.02 mmol) and NaOH (0.20 g, 5.02 mmol) in water (510 mL). The transparent reaction solution was concentrated to dryness. The solid residue was dissolved in chloroform. Dark-green crystals of complex **5b** precipitated from the solution upon prolonged storage.

B. A warm transparent solution of 4-*tert*-butyl-2,6-diformylphenol (618 mg, 3.00 mmol) in ethanol (50 mL) was added to a suspension of 1,3-diaminopropane (0.25 mL, 3.00 mmol) and $CuCl_2 \cdot 2H_2O$ (513 mg, 3.00 mmol) in ethanol (12 mL). The reaction mixture was refluxed for 7 h and then concentrated under atmospheric pressure until the precipitate started to form. Then tetrahydrofuran (100 mL) was added. The precipitate that formed was filtered off and recrystallized from water. Dark-green crystals of **5b** were obtained in a yield of 0.51 g (50%). Complex **5b**, t.decomp. >290 °C. Found (%): C, 51.47; H, 5.51; N, 7.99. $C_{30}H_{38}Cl_2Cu_2N_4O_2 \cdot H_2O$. Calculated (%): C, 51.28; H, 5.73; N, 7.93. IR (KBr), ν/cm^{-1}: 1639 (C=N). MS (MALDI-TOF), *m/z*: 611 $[LCu_2 - H]^+$, 489 $[L + 3 H]^+$, 371 $[L - 2 (57)]^+$.

Bis(trimethylacetato)(μ$_2$-14,29-di-*tert*-butyl-3,10,18,25-tetraazapentacyclo[25.3.1.1^{12,16}.0^{4,9}.0^{19,24}]dotriaconta-1(31),2,4,6,8,10,12,14,16(32),17,19,21,23,25,27,29-tetradecaene-31,32-diolato-*N*,*N*´,*O*)-dicopper(II) (7). Copper(II) trimethylacetate (101 mg, 0.38 mmol) was added to a solution of Schiff base **6** (104 mg, 0.19 mmol) in $CHCl_3$ (5 mL), where it very rapidly dissolved. After several minutes, the precipitate that formed was filtered off. The yield of complex **7** was 169 mg (100%). The product was recrystallized from an EtOH—MeOH—$CHCl_3$ mixture. Crystals suitable for X-ray diffraction study were grown by slowly evaporation of a solution of **7** in an EtOH—$CHCl_3$ mixture. Complex **7**, t.decomp. >300 °C. Found (%): C, 57.97; H, 6.44; N, 5.63. $C_{46}H_{56}Cu_2N_4O_6 \cdot 3H_2O \cdot MeOH$. Calculated (%): C, 57.95; H, 6.82; N, 5.75. IR (in oil), ν/cm^{-1}: 1620 (C=N), 1710 (C=O), 3200 (N—H). MS (MALDI-TOF), *m/z*: 681.8 $[LCu_2 - 4 H]^+$, 620.2 $[LCu - 2 H]^+$.

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