Structure of Dicopper Complexes of *N*,*N*,*N*′,*N*′-Tetrakis[(2-benzimidazolyl)methyl]-2-hydroxy-1,3-diaminopropane with Chloride Counterions

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The structures of four dicopper complexes of binucleating ligand HL-H (*N*,*N*,*N*′,*N*′-tetrakis[(2-benzimidazolyl)-methyl]-2-hydroxy-1,3−diaminopropane) with chloride counterions were investigated by the X-ray diffraction method. In $Cu_2(HL\text{-}H)Cl_4{\cdot}2H_2O{\cdot}Et_2O{\cdot}CH_3OH$ ($a = 33.837(9)$ Å, $b = 9.648(3)$ Å, $c = 32.027(8)$ Å, $\beta = 118.82(3)^\circ$, $Z = 8$, monoclinic, $C2/2$) , **1**, one chloride is not coordinated. A square pyramidal geometry is found for both the CuN_3Cl_2 and CuN_3OCl coordination sites in which the N_3 tripodal coordination sites come from the two symmetric halves of the ligand. In $Cu_2(HL\text{-}H)Cl_4{\cdot}5H_2O{\cdot}2CH_3OH{\cdot}0.5CH_3CN$ ($a = 12.124(5)$ Å, $b = 14.354(5)$ Å, $c = 16.361(6)$ Å, $\alpha = 67.52(3)^\circ$, $\beta = 89.97(3)^\circ$, $\gamma = 65.77(3)^\circ$, $Z = 2$, triclinic, $P\bar{1}$), **2**, which was obtained from the same solution as that for **1** on addition of sodium azide, the basic coordination environments of the two copper ions are the same as in **1**: CuN_3Cl_2 and CuN_3OCl in square pyramidal geometry. **1** and **2** are rotational isomers. In $Cu_2(HL\text{-}H)Cl_2(ClO_4)_2{\cdot}1.5Et_2O{\cdot}CH_3OH$ ($a = 11.684(4)$ Å, $b = 13.543(5)$ Å, $c = 17.750(7)$ Å, $\alpha = 110.78(4)^\circ$, $\beta = 72.63(3)^\circ$, $\gamma = 109.67(3)^\circ$, $Z = 2$, triclinic, $P\bar{1}$), **3**, the complex exists as a dimer; the two monomers are connected by two bridging chloride ions. The basic coordination environments of the two copper ions are square pyramidal CuN_3Cl_2 and CuN_3OCl. In $Cu_2(HL\text{-}H)Cl_2(ClO_4)_2{\cdot}5H_2O{\cdot}Et_2O{\cdot}C_2H_5OH$ ($a = 11.70(2)$ Å, $b = 14.65(3)$ Å, $c = 19.45(4)$ Å, $\alpha = 100.2(2)^\circ$, $\beta = 105.7(1)^\circ$, $\gamma = 107.0(2)^\circ$, $Z = 2$, triclinic, $P\bar{1}$), **4**, the coordination of both copper ions is CuN_3OCl; the hydroxy group bridges between two copper ions. However, the geometries of the two copper ions are distinct; one is square pyramidal, and the other is distorted trigonal bipyramidal. Together with the known structures of dicopper complexes of HL-Et, HL-H types of ligands are obviously flexible. The distances between the two copper ions in each monomer are in the range 4.9−7.2 Å. All copper ions in **1−4** are pentacoordinate. This tendency of tripodal N_3 coordinated Cu(II) to form pentacoordinate Cu(II) is used to rationalize the structures of **1−4**. The endogenous hydroxy groups in **1−4** do not deprotonate. **1−4** are the first reported structurally characterized examples of coordination of nondeprotonated alcoholic hydroxy groups to Cu(II) in dicopper complexes. In **4**, the hydroxy group even bridges between two Cu(II) ions.

Introduction

Hemocyanins (Hc) are copper-containing proteins which bind O_2 cooperatively;[1,2] they serve as O_2 carriers for many mollusks and arthropods. The three-dimensional structure of *Panulirus interruptus* Hc[3] indicates that each copper is coordinated by three histidines; the Cu−Cu distance is 3.8 ± 0.4 Å. However crystallographic studies at 3.2 Å resolution do not allow statements regarding the presence or absence of a small ligand, such as a *μ*-hydroxo group, bridging the copper ions. The electron density distribution shows no evidence for an amino-acid side chain functioning as a bridging ligand. Small ions such as SCN^-, N_3^-, Cl^-, and F^-, have been incorporated into Hc to probe the structural and spectral changes of Hc.[4−8] To mimic the structural, magnetic, and oxygen-binding properties of hemocyanin, a large number of binuclear ligands and their copper(II) complexes were synthesized and characterized. These binuclear model complexes can be roughly divided into three categories according to the nature of the endogenous bridging ligand. In the first group, the binuclear ligand contains a phenoxo group that bridges two copper ions.[9−23] In the second group, an alkoxo group bridges two copper ions.[24−28] In the

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other group, there is no bridging endogenous group.[29-35] Examples of complexes containing dioxygen, which coordinate to two Cu(II) ions in either a trans-μ_2[36] or μ_2:η^2:η^2 [37-42] mode serving as the sole element to bring two mononuclear Cu(II) complexes to form binuclear copper(II) complexes, are also known. μ_2:η^2:η^2-O_2 dicopper(II) complexes serve as models for oxyhemocyanin; they reproduce the gross spectral features of oxyhemocyanin. As for the complexes of binucleating ligands, some phenoxo-bridged dicopper complexes can reproduce the nearly diamagnetic property at room temperature of met-hemocyanin with a bridging exogenous azido group. Concerning the second group of model compounds, Reed et al.[24-26] reported that the binuclear copper(II) complex of *N,N,N′,N′*-tetrakis[2-(1-ethylbenzimidazolyl)methyl]-2-hydroxy-1,3-diaminopropane (HL-Et) with an exogenous azide bridging ligand has two features remarkably similar to that of azido-met-hemocyanin. It is diamagnetic at room temperature, and the Cu(II)−Cu(II) distance 3.65 Å closely matches the distance 3.6−3.7 Å in met-hemocyanin. These binucleating ligands are of interest intrinsically. We wish to gain a better understanding of the fundamental chemistry of the endogenous alkoxo group. Here we report the structures of dicopper complexes of *N,N,N′,N′*-tetrakis[(2-benzimidazolyl)methyl]-2-hydroxy-1,3-diaminopropane (HL-H) with chlorides as counterions. The endogenous alkoxo group does not deprotonate and can function as either a terminal or a bridging ligand. Together with the ethyl-substituted ligand HL-Et, a ligand of this type is remarkably flexible in forming a dicopper complex. The nature of the counterions, whether they act as bridging ligands, has a profound influence on the structure of the resulting dicopper complex.

Experimental Section

The reagents used in this work were G.R. grade; they were used directly without further purification. These reagents were obtained from various sources: 1,2-diaminobenzene and $CuCl_2{\cdot}2H_2O$ from Merck; $Cu(ClO_4)_2{\cdot}6H_2O$ from Aldrich; NaN_3 from Janssen; 2-hydroxy-1,3-diaminopropanetetraacetic acid from Sigma. Elemental analysis results were obtained on a Perkin-Elmer 240C-2400 EA instrument. Atomic absorption spectra were obtained on a Varian AA-20 spectrometer to determine the copper content. ^1H NMR spectra were recorded on a Varian Unity-400 spectrometer. IR spectra were measured on a Bomen DA-3002 FTIR spectrometer with Nujol as diluent. Variable-temperature magnetic susceptibility was measured on a Quantum Design Mpms Squid magnetometer operated at 0.3 T.

Preparation of *N,N,N′,N′*-tetrakis[(2-benzimidazolyl)methyl]-2-hydroxy-1,3-diaminopropane (denoted as HL-H). This potentially heptadentate ligand was synthesized according to the literature procedure.[25] Briefly, it was prepared from the reaction between 1,2-diaminobenzene and 2-hydroxy-1,3-diaminopropanetetraacetic acid at 170−180 °C for 1 h. The mixture was then dissolved in 4 M hydrochloric acid and subsequently neutralized with dilute aqueous ammonia. The off-white precipitate which was the crude product denoted HL-H·*n*HCl, contained ca. 5% hydrogen chloride. Recrystallization from ethanol or methanol reduced the chlorine content to ca. 1.3%. Pure HL-H was obtained after recrystallization from methanol or ethanol at least three times. Alternatively, we found that when NaOH was used instead of aqueous ammonia in the synthesis, the precipitate is pure HL-H with chlorine content less than 0.01% without further purification. It was identified by ^1H NMR ($(CD_3)_2SO$/ppm): 2.559 (2H, dd; 13.28 Hz, 7.56 Hz), 2.792 (2H, dd; 13.28 Hz, 4.12 Hz), 4.146, 4.180 (8H, AB quartet, 15.72 Hz), 4.16 (1H, m, overlap with the AB quartet), 7.20 (8H, m), 7.55 (8H, m). IR (Nujol/cm^{-1}): 1081 (ν(C−O)). Anal. Found (calc) for HL-H·$4H_2O$ ($C_{35}H_{42}N_{10}O_5$): C, 61.68 (61.57), H, 6.05 (6.20), O, 11.47 (11.72), N, 20.20 (20.51).

Preparation of Cu_2(HL-H)Cl_4. A 5 mL methanol solution of $CuCl_2{\cdot}2H_2O$ (0.2855 g, 1.67 mmol) was added slowly to a methanol solution (170 mL) of crude HL-H·*n*HCl (0.51g, 0.84 mmol) under constant stirring. One-quarter of the reaction mixture was evaporated to 20 mL. This concentrated solution was used to grow a single crystal by diffusion technique using diethyl ether as diffusant. The single crystal obtained is labeled as **1**. The remaining solution was stirred until a lot of precipitate was obtained; after filtering to collect the precipitate and washing with methanol, we dried the precipitate at 50 °C in a vacuum oven. IR (Nujol/cm^{-1}): 1075 (νC-O)). Anal. Found (calc) for Cu_2(HL-H) $Cl_4{\cdot}4.5\ H_2O$ ($Cu_2C_{35}H_{43}N_{10}O_{5.5}Cl_4$): Cu, 12.5 (13.25); C, 43.96 (43.76); H, 4.44 (4.51); N, 14.71 (14.58); O, 9.48 (9.16); Cl, 14.91 (14.76). Alternatively Cu_2(HL-H)Cl_4 in another crystalline form was prepared according to the following procedure. A 20 mL methanol solution of $CuCl_2{\cdot}2H_2O$ (0.56 g, 3.28 mmol) was added slowly to a 390 mL methanol solution of crude HL-H·*n*HCl (1g, 1.64 mmol) under constant stirring. After continued stirring for 30 min, a

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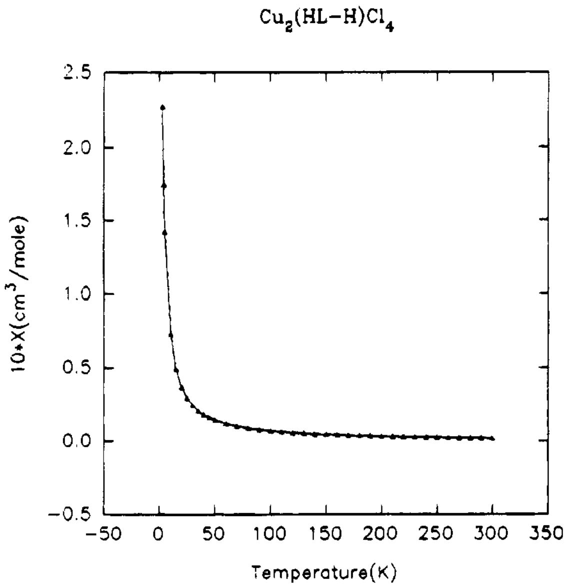

Figure 1. Magnetic susceptibility of **1** at 0.3 T as a function of temperature. The solid curve is the results of least-squares analysis according to eq 1.

5 mL methanol solution of NaN_3 (0.2187 g, 3.36 mmol) was added to the reaction mixture. The solution was left to evaporate to a volume of ca. 150 mL. A small portion (3 mL), after addition of 1 mL of acetonitrile, was used to grow a single crystal by the solvent diffusion technique using diethyl ether as diffusant. This single crystal was labeled **2**. After being dried in a vacuum oven at 50 °C, the precipitate obtained following further reduction of the volume of the remaining reaction mixture had the same elemental analysis results as that used to prepare **1**.

Preparation of Cu_2(HL-H) Cl_2 $(ClO_4)_2$. A 20 mL methanol solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (1.22 g, 3.29 mmol) was added slowly to a 220 mL methanol solution of crude HL-H·*n*HCl (0.95 g, 1.56 mmol) with stirring. The mixture was evaporate to 30 mL with stirring. A small portion (ca 6 mL) was used to grow a single crystal using the solvent diffusion method with diethyl ether as diffusant. This single crystal was labeled as **3**. The volume of the remaining mixture was reduced further by solvent evaporation until a precipitate of the product was obtained. This precipitate was collected, washed with ethanol, and dried in a 50 °C vacuum oven. Anal. Found (calc) for Cu_2(HL-H)$Cl_2(ClO_4)_2{\cdot}4.5H_2O$ ($Cu_2C_{35}H_{43}N_{10}O_{13.5}Cl_4$): Cu, 11.54 (11.67); C, 39.17 (38.61); H, 3.90 (3.98); N, 12.57 (12.87); O, 19.51 (19.84); Cl, 13.30 (13.03). Another crystalline form of the same complex was obtained by the following procedure. A 20 mL ethanol solution of $Cu(ClO_4)_2$ $\cdot 6H_2O$ (1.261 g, 3.4 mmol) was added slowly to the 400 mL ethanol solution of HL-H·*n*HCl (1 g, 1.64 mmol) which also contained 0.227 mL (1.64 mmol) of triethylamine. The solvent was evaporated under stirring until the volume of the reaction mixture was reduced to 150 mL. A small portion was used for single crystal growing using the solvent diffusion technique employing diethyl ether as diffusant. The crystal thus obtained was labeled **4**. The precipitate obtained following further reduction of the volume of the remaining reaction mixture had the same elemental analysis results as that used to prepare **3**.

Magnetic susceptibility measurements of the vacuum oven dried sample of **1** were carried out in the temperature range 4.2−300 K. The resulting data (Figure 1) were analyzed according to eq 1,[25,43] where *p*

$$\chi = 2(Ng^2\beta^2/kT)[(1-p)/\{3+\exp(-2J/kT)\}+p/4] + \mathrm{TIP} + \chi_0 \quad (1)$$

is the percentage of mononuclear copper complex and TIP is the temperature independent paramagnetism. Analysis by nonlinear least-squares fitting yielded $g = 2.000(3)$, $J = -0.36(1)$ cm^{-1}, TIP + $\chi_0 = -6.2(5) \times 10^{-4}$, and *p* is practically zero.

X-ray Crystallography. Single crystals of **1**−**4** were each sealed in epoxy resin to prevent loss of coordinating solvent that led to breakdown of the crystals. Diffraction intensity data were collected on a Enraf-Nonius CAD-4 four-circle diffractometer using monochromatic Mo Kα radiation (0.709 30 Å) from a graphite single crystal at 23 °C. The general data collection and results are summarized in Table 1. The initial phase was determined by the heavy-atom method. All non-hydrogen atoms were subsequently located from a Fourier map and then anisotropically refined by full-matrix least squares. All hydrogen atoms were placed in ideal positions in structure factor calculations. R and Rw values after least-squares refinement are reported in Table 1. All calculations were performed on a Micro VAX III computer with NRCC-SDP-VAX programs.

Results and Discussion

The ligand *N,N,N′,N′*-tetrakis[(2-benzimidazolyl)methyl]-2-hydroxy-1,3-diaminopropane (denoted as HL-H) was synthesized according to the literature method.[25] However, we found that the original assignment of the ^1H NMR spectrum was incomplete. The two protons of the methylene groups in the 2-hydroxy-1,3-diaminopropane part are inequivalent; δ values are 2.559 and 2.792 ppm. The two protons in the methylene groups in the benzimidazolylmethyl groups are also inequivalent; they form an AB pattern at 4.146 and 4.180 ppm with *J* = 15.72 Hz. The signal of the proton bonded to carbon carrying the hydroxy group is buried inside the AB pattern; it was detected only from the integrated signal intensity.

A single crystal of each of the four dicopper(II) complexes of HL-H was obtained according to simple reactions between the copper(II) salt and HL-H ligand as outlined:

$$CuCl_2 + \text{HL-H}{\cdot}n\text{HCl} \xrightarrow[Et_2O]{MeOH} \underset{\mathbf{2}}{Cu_2(\text{HL-H})Cl_4{\cdot}2H_2O{\cdot}Et_2O{\cdot}CH_3OH}$$

$$CuCl_2 + \text{HL-H}{\cdot}nHCl \xrightarrow[Et_2O]{N_3^- + MeOH + CH_3CN} \underset{\mathbf{2}}{Cu_2(\text{HL-H})Cl_4{\cdot}5H_2O{\cdot}2CH_3OH{\cdot}0.5CH_3CN}$$

$$Cu(ClO_4)_2 + \text{HL-H}{\cdot}nHCl \xrightarrow[Et_2O]{MeOH} \underset{\mathbf{3}}{Cu_2(\text{HL-H})Cl_2(ClO_4)_2{\cdot}1.5Et_2O{\cdot}CH_3OH}$$

$$Cu(ClO_4)_2 + \text{HL-H}{\cdot}n\text{HCl} \xrightarrow[Et_2O]{NEt_3 + EtOH} \underset{\mathbf{4}}{Cu_2(\text{HL-H})Cl_2(ClO_4)_2{\cdot}5H_2O{\cdot}Et_2O{\cdot}C_2H_5OH}$$

The geometry of the pentacoordinate Cu(II) site, as encountered in this work, is most likely either distorted square-pyramidal (SP) or distorted trigonal-bipyramidal (TBP). It is difficult to assign which is the more relevant description of the coordinating polyhedron. The approach of Mutterties and Guggenberger,[44] which compares the actual geometry to the ideal geometries by way of a key shape-determining dihedral angle, is a convenient method in deciding which geometry is more appropriate. In the pentacoordinated geometry, the key dihedral angle is e_3, which has values of 53.1° and 0.0° for TBP and SP respectively.

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Table 1. Summary of Crystal Data and Intensity Collection Conditions of Single Crystals **1**−**4**

	complex			
	1	**2**	**3**	**4**
formula	$Cu_2C_{40}H_{52}N_{10}O_5Cl_4$	$Cu_2C_{38}H_{53.5}N_{10.5}O_8Cl_4$	$Cu_2C_{42}H_{53}N_{10}O_{11.5}Cl_4$	$Cu_2C_{41}H_{60}N_{10}O_{16}Cl_4$
a, Å	33.837(9)	12.124(5)	11.683(4)	11.70(2)
b, Å	9.684(3)	14.354(5)	13.543(5)	14.65(3)
c, Å	32.027(8)	16.361(6)	17.750(7)	19.45(4)
α, deg	90	67.52(3)	110.78(4)	100.2(2)
β, deg	118.82(3)	89.97(3)	72.63(3)	105.7(1)
γ, deg	90	65.77(3)	109.67(3)	107.0(2)
V, $Å^3$	9195(4)	2357.5(15)	2420.8(16)	2948(10)
Z	8	2	2	2
fw	1030.79	1035.76	1128.66	1171.5
space group	$C2/c$ (No. 15)	$P\bar{1}$ (No. 1)	$P\bar{1}$ (No. 1)	$P\bar{1}$ (No. 1)
T, °C	25	25	25	25
λ, Å	0.709 30	0.709 30	0.709 30	0.709 30
ϱ_{calc}, g cm^{-3}	1.489	1.459	1.548	1.32
μ, cm^{-1}	12.1	10.6	11.8	9.7
$R(F_o)$,[a] %*	5.1	5.8	5.8	10.2
$R_w(F_o)$,[a] %	4.4	5.1	6.5	13.4

[a] The weighted and unweighted residuals are defined as $R(F_o) = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$ and $R_w(F_o) = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2}$, with $w = 1/\sigma(F)$.

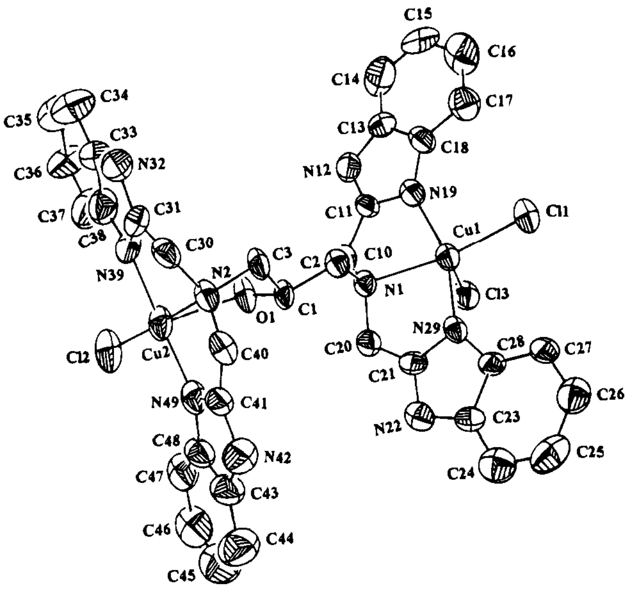

Figure 2. ORTEP drawing of $Cu_2(HL\text{-}H)Cl_4{\cdot}2H_2O{\cdot}Et_2O{\cdot}CH_3OH$, **1**. For clarity, solvent molecules and hydrogen atoms are omitted.

Structure of $Cu_2(HL\text{-}H)Cl_4{\cdot}2H_2O{\cdot}Et_2O{\cdot}CH_3OH$, 1. The structure of this tetrachloride complex is shown in Figure 2. Atomic coordinates of significant atoms are given in Table 2; selected bond distances and bond angles are given in Tables 3 and 4. The shape-determining angle e_3 is also included in Table 3. Cu1 is pentacoordinated; its coordination sphere consists of three nitrogen atoms and two chlorides. Cu2, also pentacoordinated, is surrounded by three nitrogen atoms, one oxygen atom, and one chloride. The fourth chloride is not coordinated to any copper ion. The hydroxy proton in HL-H does not dissociate in the complex. The shape-determining dihedral angle (e_3) between the N1−Cl1−N19 and N1−Cl1−N29 planes is 9.9°. Hence Cu1 is in a slightly distorted square pyramidal coordination environment. Each basal atom (N1, N19, Cl1, and N29) is no more than 0.1 Å away from the least-squares plane passing through them. Cl3 is at the axial position. Cu1 is 0.306 Å above the basal plane toward Cl3. As ∠N1−Cu1−N19 and ∠N1−Cu1−N29 are about 80° and ∠N19−Cu1−Cl1 and ∠N29−Cu1−Cl1 are about 98°, Cu1 is evidently off the center of the basal plane and near Cl1. For Cu2, the shape-determining dihedral angle (e_3) between the N2−Cl2−N39 and N2−Cl2−N49 planes is 4.9°. Therefore, Cu2 is also in a square pyramidal coordination environment. All basal atoms (N2, N39, Cl2, and N49) are within 0.1 Å of the least-squares plane passing through them. Cu2 is 0.123 Å above the basal plane toward the axial ligating atom O1. The angles between Cu2 and the basal coordinating atoms are divided into two groups: one is near 81° (∠N2−Cu2−N39 and ∠N2−Cu2−N49), and the other is near 98° (∠Cl2−Cu2−N39 and ∠Cl2−Cu2−N49). Cu2 is not located along the center axis of the basal plane but bends toward Cl2. The Cu1−Cu2 distance is 7.273 Å. The interaction between the copper ions is expected to be weak. The vanishingly small J value of -0.36 cm^{-1} obtained from magnetic susceptibility measurement is consistent with the lack of interaction between the copper ions.

A notable feature of **1** is that the hydroxy proton does not dissociate when OH coordinates to the Cu(II) ion. Although there is one precedent in which the undissociated proton was reported in a dicopper(II) complex of HL-Et,[25] **1** is the first structurally characterized example of this coordination mode for dicopper complexes of HL-R (R = H, Et). On the other hand, there are complexes with known crystal structures in which alcoholic groups in polydentate ligands do not coordinate to copper[27,45] or iron.[46] In complexes **2**−**4** reported below, like **1** the protons of coordinated alcoholic groups do not dissociate.

Structure of $Cu_2(HL\text{-}H)Cl_4{\cdot}5H_2O{\cdot}2CH_3OH{\cdot}0.5CH_3CN$, 2. This single crystal was grown in a solution similar to that used to prepare **1** with the presence of additional sodium azide. Although azide ion was not incorporated into **2** as a bridging ligand, a new crystal form was obtained. The structure of **2** is shown in Figure 3. Atomic coordinates of significant atoms are given in Table 5; selected bond distances, e_3, and bond angles are given in Tables 3 and 4. Cu1 is coordinated by three nitrogen atoms and two chlorides. Cu2 is also pentacoordinate: its coordination sphere consists of three nitrogen atoms, one oxygen atom, and one chloride; one chloride coordinates to no copper.

According to data in Tables 3 and 4, the coordination environment of Cu1 in **2** resembles that of Cu1 in **1**. Similarities of the coordination environments of Cu2 in **2** and Cu2 in **1** are also notable. Rotations about the C1−C2 and C2−N1 axes can bring the structure of **2** into a structure nearly that of **1**.

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Table 2. Atomic Coordinates *x*, *y*, *z* and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for Non-Hydrogen Atoms of the Cation of $Cu_2(HL\text{-}H)Cl_4{\cdot}2H_2O{\cdot}Et_2O{\cdot}CH_3OH$, **1**

	x	*y*	*z*	U_{eq}		*x*	*y*	*z*	U_{eq}
Cu1	0.70012(3)	0.39984(9)	0.25385(3)	34(1)	C25	0.9006(3)	0.4129(9)	0.3782(3)	63(6)
Cu2	0.71969(3)	0.27778(10)	0.04049(3)	42(1)	C26	0.8696(3)	0.3483(8)	0.3891(3)	52(6)
Cl1	0.70623(6)	0.29070(21)	0.31889(6)	44(1)	C27	0.82410(23)	0.3472(7)	0.35800(23)	38(5)
Cl2	0.69527(8)	0.43440(22)	−0.01786(7)	61(17)	C28	0.80968(22)	0.4117(7)	0.31406(22)	33(5)
Cl3	0.68487(7)	0.65126(20)	0.26087(6)	45(1)	N29	0.76628(18)	0.4244(5)	0.27529(17)	32(3)
Cl4	0.44162(11)	0.4145(4)	0.01820(12)	138(3)	C30	0.7281(3)	−0.0128(7)	0.06462(25)	43(6)
N1	0.69664(18)	0.4327(5)	0.18648(17)	30(3)	C31	0.68225(24)	0.0161(8)	0.02563(23)	43(6)
N2	0.74420(18)	0.1191(6)	0.09176(18)	35(3)	N32	0.64853(21)	−0.0735(6)	0.00513(20)	52(5)
C1	0.72094(23)	0.2875(7)	0.13479(21)	32(5)	C33	0.6113(3)	−0.0024(8)	−0.0290(3)	56(6)
C2	0.70347(23)	0.2924(7)	0.17113(22)	33(5)	C34	0.5682(3)	−0.0467(10)	−0.0587(3)	81(7)
C3	0.72255(23)	0.1360(7)	0.12242(22)	35(5)	C35	0.5392(3)	0.0514(11)	−0.0868(3)	99(8)
C10	0.65169(23)	0.4900(7)	0.15602(23)	38(5)	C36	0.5526(3)	0.1889(11)	−0.0859(3)	92(8)
C11	0.62053(23)	0.4193(7)	0.1609(23)	34(5)	C37	0.5964(3)	0.2317(9)	−0.0556(3)	72(7)
N12	0.57595(19)	0.4125(6)	0.14074(18)	43(5)	C38	0.6261(3)	0.1336(8)	−0.02686(24)	53(6)
C13	0.55968(23)	0.3402(8)	0.16596(24)	46(5)	N39	0.67126(19)	0.1431(6)	0.00786(18)	42(5)
C14	0.5162(3)	0.3020(10)	0.1533(3)	72(7)	C40	0.79351(23)	0.1274(8)	0.11909(24)	42(6)
C15	0.5108(3)	0.2262(10)	0.1866(3)	82(8)	C41	0.80765(23)	0.2688(8)	0.11369(23)	41(6)
C16	0.5477(3)	0.1934(10)	0.2308(3)	72(7)	N42	0.84880(21)	0.3207(7)	0.13990(21)	54(5)
C17	0.5908(3)	0.2323(8)	0.2431(3)	54(6)	C43	0.8481(3)	0.4531(8)	0.1239(3)	54(6)
C18	0.59638(24)	0.3076(7)	0.20900(24)	42(5)	C44	0.8813(3)	0.5518(10)	0.1381(3)	80(7)
N19	0.63554(18)	0.3588(6)	0.21001(18)	35(3)	C45	0.8683(3)	0.6764(9)	0.1140(3)	91(8)
C20	0.73366(23)	0.5302(7)	0.19657(23)	37(5)	C46	0.8252(3)	0.7008(9)	0.0781(3)	75(8)
C21	0.77218(23)	0.4927(7)	0.24285(23)	34(5)	C47	0.7923(3)	0.6007(8)	0.0641(3)	58(7)
N22	0.81554(19)	0.5255(6)	0.25792(19)	39(5)	C48	0.8049(3)	0.4750(8)	0.0879(3)	48(6)
C23	0.84008(23)	0.4755(7)	0.30327(23)	37(5)	N49	0.77950(19)	0.3545(6)	0.08149(19)	42(5)
C24	0.8858(3)	0.4772(8)	0.3353(3)	56(6)	O1	0.69301(16)	0.3623(5)	0.09253(15)	42(3)

Table 3. Selected Bond Distances (Å) and the Shape-Determining Dihedral Angles e_3 (deg) of Complexes **1**−**4**

	coord site of **1**		coord site of **2**		coord site of **3**		coord site of **4**	
	N_3Cl_2	N_3OCl	N_3Cl_2	N_3OCl	N_3Cl_2[a]	N_3OCl	N_3OCl	N_3OCl
Cu1−N1	2.128(5)		2.214(6)		2.106(8)		2.04(2)	
Cu2−N2		2.106(5)		2.100(7)		2.116(8)		2.14(2)
Cu1−N19	1.987(6)		1.933(7)		1.953(8)		1.90(3)	
Cu1−N29	2.014(5)		1.947(7)		1.963(9)		1.96(2)	
Cu2−N39		1.956(6)		1.965(7)		1.953(9)		1.97(3)
Cu2−N49		1.952(6)		1.948(7)		1.975(9)		1.92(3)
Cu1−Cl1	2.255(2)		2.309(3)		2.237(3)		1.94(2)	
Cu1−Cl3	2.521(2)		2.481(3)		2.846(4)		2.41(2)[d]	
Cu2−Cl2		2.233(2)		2.240(3)		2.241(3)		2.231(9)
Cu2−O1		2.390(4)		2.322(5)		2.351(7)		2.72(2)
Cu1−Cu2	7.273(2)		6.299(3)		7.182(4)		4.94(1)	
e_3[b]	9.9(3)	4.9(3)	8.9(4)	6.1(4)	3.2(5)	14.8(5)	38.0(14)	0.8(16)
d[c]	0.306(3)	0.123(3)	0.373(4)	0.101(4)	0.099(4)	0.047(4)		0.05(1)

[a] To be consistent with the molecular structural labeling in Figure 3, all Cl3 in the bond distances labeling should be changed to Cl1A. [b] The shape-determining dihedral angle between the N1−Cl1−N19 and N1−Cl1−N29, or between the N2−Cl2−N39 and N2−Cl2−N49 planes. [c] The distance between copper ions and the least-squares plane passing through the four basal coordinating atoms. [d] This distance is between Cu1 and O1 because there is no Cl3 in this complex.

Therefore if one neglects the small variations that may be due to crystal packing and the presence of various coordinating solvent molecules, **1** and **2** can be considered as rotational isomers.

Structure of $Cu_2(HL\text{-}H)Cl_2(ClO_4)_2{\cdot}1.5Et_2O{\cdot}CH_3OH$, 3. The structure of **3** appears in Figure 4. Atomic coordinates of significant atoms are presented in Table 6; selected bond distances, e_3, and bond angles are given in Tables 3 and 4. The compound exists in the crystal as a dimer with inversion symmetry. Cu1 is pentacoordinate; its coordination sphere consists of three nitrogen atoms and two bridging chlorides. Cu2 is also pentacoordinate: it is surrounded by three nitrogen atoms, one oxygen and one chloride. Unlike **1** and **2**, all chlorides are coordinated to copper ions. For Cu1 the shape-determining dihedral angle (e_3) between the N1−Cl1−N19 and N1−Cl1−N29 planes is 3.2°. Hence, Cu1 has square-pyramidal coordination. The four basal atoms (N1, N19, Cl1, and N29) are within 0.03 Å of the least-squares planes passing them. Cu1 is 0.1 Å above the basal plane toward the axial Cl1A. Examining the coordination of Cl1 and Cl1A to Cu1A shows that Cl1A is clearly in the basal plane and Cl1 at the axial position; their roles are switched when coordinated to Cu1. Apart from the exceptional large Cu1−Cl1A distance, other structural features about Cu1 resemble those of Cu1 in **1** and **2**. For Cu2, the shape-determining dihedral angle (e_3) between the N2−Cl2−N39 and N2−Cl2−N49 planes is 14.5°. This value, although larger than those for Cu1 in **1** and **2**, remains nearer the ideal SP geometry than to that of TBP. Therefore, Cu2 has distorted square pyramidal coordination. In spite of the large e_3, the bond distances and angles about Cu2 are near those found for Cu2 in **1** and **2**.

Comparison of the Cu−chloride(axial) distances in SP coordination geometries in **1** and **2** indicates that Cu1-Cl1A in **3** is particularly long. This condition correlates with the small e_3 angle. The bridging coordination mode of Cl1A may also contribute to the lengthening of the Cu1−Cl1A bond.

Structure of $Cu_2(HL\text{-}H)Cl_2(ClO_4)_2{\cdot}5H_2O{\cdot}Et_2O{\cdot}C_2H_5OH$, 4. A single crystal of this complex was grown in the presence of triethylamine which was intended, but failed, to extract the proton from the hydroxy group of HL-H. The structure of this

Table 4. Selected Bond Angles (deg) of Compounds **1−4**

	coord site of **1**		coord site of **2**		coord site of **3**		coord site of **4**	
	N_3Cl_2	N_3OCl	N_3Cl_2	N_3OCl	N_3Cl_2[a]	N_3OCl	N_3OCl[b]	N_3OCl
N1−Cu1−N19	79.0(2)		80.7(3)		81.4(3)		82.9(9)	
N1−Cu1−N29	80.6(2)		79.6(3)		81.0(3)		83.6(9)	
N1−Cu1−Cl1	160.5(2)		158.1(2)		173.8(3)		172(1)	
N1−Cu1−Cl3	91.8(2)		102.9(2)		88.2(3)		82.0(8)	
N2−Cu2−N39		81.0(2)		80.0(3)		81.3(3)		82(1)
N2−Cu2−N49		82.1(2)		83.2(3)		82.3(3)		82(1)
N2−Cu2−Cl2		175.0(2)		176.6(2)		177.6(2)		177.3(7)
N2−Cu2−O1		81.1(2)		80.3(2)		80.7(3)		78.6(8)
N19−Cu1−N29	158.1(2)		156.3(3)		162.2(4)		146(1)	
N39−Cu2−N49		160.6(3)		150.8(3)		159.3(4)		164(1)
N19−Cu1−Cl1	98.0(2)		96.5(2)		98.6(3)		100(1)	
N19−Cu1−Cl3	93.1(2)		95.8(2)		90.8(3)		104.1(9)	
N29−Cu1−Cl1	98.5(2)		96.8(2)		98.5(3)		98.1(9)	
N29−Cu1−Cl3	95.6(2)		101.3(2)		91.4(3)		104.7(9)	
Cl1−Cu1−Cl3	107.6(1)		98.9(1)		98.1(1)		90.2(8)	
N39−Cu2−Cl2		97.4(2)		98.1(2)		98.0(3)		96.8(8)
N49−Cu2−Cl2		98.6(2)		99.7(2)		98.8(3)		98.7(8)
N39−Cu2−O1		95.7(2)		102.1(2)		100.3(3)		96.6(9)
N49−Cu2−O1		91.1(2)		98.3(2)		89.5(3)		83.6(9)
Cl2−Cu2−O1		103.8(1)		97.4(2)		97.2(2)		104.1(5)
C1−O1−Cu1							100(2)	

[a] All angle labeling with Cl3 should be changed to Cl1A to be consistent with the labeling in Figure 3. [b] Because the coordination site is N_3OCl, the labeling of structural data with Cl3 should be replaced with O1.

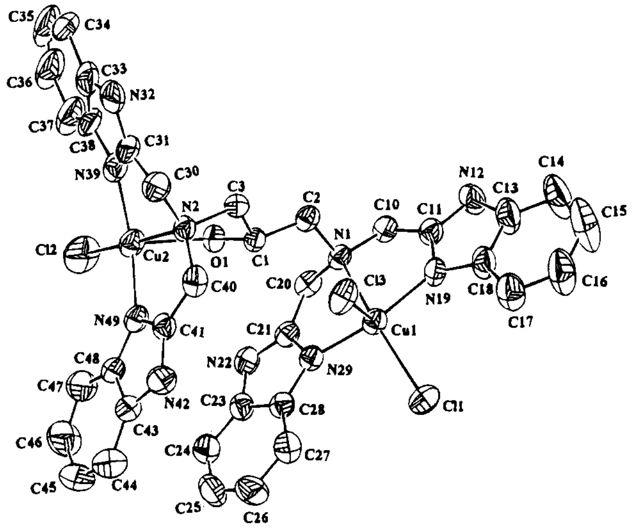

Figure 3. ORTEP drawing of $Cu_2(HL\text{-}H)Cl_4\cdot5H_2O\cdot2CH_3OH\cdot0.5CH_3CN$, **2**. For clarity, solvent molecules and hydrogen atoms are omitted.

dichloride diperchlorate is shown in Figure 5. Atomic coordinates of significant atoms are given in Table 7; selected bond distances, e_3, and bond angles appear in Tables 3 and 4. Cu1 is pentacoordinate, surrounded by three nitrogen atoms, one oxygen atom, and one chloride. Cu2 is also pentacoordinate; its coordination sphere consists also of three nitrogen atoms, one oxygen, and one chloride. For Cu1, e_3 is 38°, which approaches the ideal value of 53° for TBP. Hence, Cu1 is reasonably assigned to have distorted trigonal bipyramidal coordination. As ∠N1−Cu1−Cl1 is 172°, N1 and Cl1 are assigned to the axial positions; N19, N29, and O1 are then in the trigonal basal plane. The angles between the basal atoms and Cu1 are 146° (∠N19-Cu1-N29) and 105° (∠N19−Cu1−O1 and ∠N29−Cu1−O1); they are severely distorted from the ideal 120°. The bond angles between N1 and the equatorial atoms about Cu1 are between 82 and 83°. These values indicate clearly that Cu1 is not in the trigonal plane but leans toward the other axial atom Cl1. The angles between the axial chloride Cl1 and the equatorial atoms around Cu1 are larger than 90°; N19−Cu1−Cl1 and N29−Cu1−Cl1 approach 100°. These angles attest to the fact that Cu1 is not in the trigonal plane. For Cu2, e_3, is 0.8°, which is the smallest angle in Table 2; therefore Cu2 has a square pyramidal coordination. The four basal atoms (N2, N39, Cl2, and N49) are within 0.01 Å of the least-squares plane passing through them. Cu2 is 0.05 Å above the basal plane and leans toward axial ligating atom O1. As ∠N2−Cu2−N39 and ∠N2−Cu2−N49 are 82°, Cu2 is obviously not located along the center axis of the basal plane.

The Cu1−Cl1 distance of 1.94 Å is smaller than any Cu−Cl distance in complexes **1−3**. The reason is that Cl1 is in the axial position of a TBP coordination geometry of Cu1. The Cu2−O1 distance is 0.3 Å greater than that of Cu1−O1; it also exceeds the Cu2−O1 distances in **1−3**. The explanation is that O1 is at the basal position of a nearly ideal SP geometry of Cu2.

The proton of the 2-hydroxy group in **4** does not dissociate, like **1−3**. However, this hydroxy group coordinates simultaneously to two copper(II) ions. **4** appears to be the first structurally characterized example of such a bonding mode of the alcoholic hydroxy group.

Comparison of Structures of 1−4. The complexes of $[Cu_2(HL\text{-}H)Cl_n]^{4-n}$, $n = 2$ and 4, exhibit varied structural features. In complex **1** or **2**, one chloride does not coordinate and the complexes with the three remaining chlorides coordinated to copper ions exist as monomers. There is no obvious interaction between the two copper ions; their coordination sites are N_3Cl_2 and N_3OCl. In **3**, the complex with both chlorides coordinated to copper ions exists as a dimer; the monomers are bridged by two chlorides. There is no interaction between the copper ions in each monomer; the coordinating sites for the copper ions are N_3Cl_2 and N_3OCl. Complex **4**, having both chlorides coordinated to copper ions, exists as a monomer. The hydroxy group serves to bridge the two copper ions; their coordination sites are both N_3OCl. Obviously, the basic coordinating sites for complexes of this series are N_3Cl_2 and N_3OCl. The e_3 dihedral angles of each dicopper complex follow a general trend that, if one is large, the other is small. The metal−ligand bond distances and angles around the CuN_3Cl_2 complexes are remarkably similar to each other. The bond distances and angles for the CuN_3OCl geometry also vary little except those in **4**. The various structural features of this series of complexes can

Table 5. Atomic Coordinates *x*, *y*, *z* and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for Non-Hydrogen Atoms of the Cation of Cu_2(HL-H)Cl_4·5H_2O·2CH_3OH·0.5CH_3CN, **2**

	x	*y*	*z*	U_{eq}		*x*	*y*	*z*	U_{eq}
Cu1	0.62272(10)	0.13373(10)	0.44619(7)	41(1)	C25	0.8959(9)	−0.3542(8)	0.6377(7)	70(8)
Cu2	0.86813(10)	−0.04770(10)	0.84940(7)	47(1)	C26	0.9180(8)	−0.2863(8)	0.5596(7)	70(8)
Cl1	0.66366(22)	0.07932(22)	0.32934(16)	57(22)	C27	0.8487(8)	−0.1712(8)	0.5212(6)	57(8)
Cl2	0.8112(3)	−0.1572(3)	0.96197(18)	85(29)	C28	0.7550(7)	−0.1263(7)	0.5635(6)	43(7)
Cl3	0.80919(21)	0.15915(22)	0.46853(15)	55(2)	N29	0.6684(6)	−0.0155(6)	0.5411(4)	39(5)
O1	0.6833(5)	0.0495(5)	0.7480(3)	44(5)	C(30)	0.9777(8)	0.1058(8)	0.7831(6)	51(8)
C1	0.7071(7)	0.119(7)	0.6650(5)	37(7)	C31	0.9175(8)	0.1178(8)	0.8608(6)	56(8)
N1	0.5203(6)	0.1785(6)	0.5481(4)	38(6)	N32	0.9213(7)	0.1840(6)	0.8989(5)	66(7)
N2	0.9117(6)	0.0632(6)	0.7431(4)	38(5)	C(33)	0.8576(9)	0.6179(8)	0.9696(6)	76(8)
C2	0.5891(7)	0.2095(7)	0.6007(5)	39(7)	C34	0.8298(10)	0.2198(9)	1.0305(7)	101(11)
C3	0.7938(7)	0.1574(7)	0.6844(5)	39(7)	C35	0.7614(11)	0.1839(10)	1.0901(7)	136(12)
C10	0.4039(7)	0.2794(7)	0.4966(6)	46(7)	C36	0.7182(10)	0.1083(10)	1.0895(7)	117(12)
C11	0.4252(7)	0.3430(7)	0.4083(6)	47(7)	C37	0.7455(9)	0.0619(9)	1.0314(6)	84(10)
N12	0.3611(6)	0.4523(6)	0.3546(5)	61(6)	C38	0.8162(8)	0.0916(8)	0.9701(6)	65(8)
C13	0.4100(8)	0.4774(8)	0.2781(6)	67(8)	N39	0.8584(6)	0.0600(6)	0.8987(5)	52(6)
C14	0.3805(9)	0.5743(9)	0.2027(7)	96(10)	C40	1.0104(7)	−0.0035(7)	0.3083(5)	44(7)
C15	0.4526(10)	0.5699(9)	0.1373(7)	113(11)	C41	0.9903(7)	0.1140(7)	0.2684(5)	39(6)
C16	0.5497(9)	0.4700(9)	0.1480(6)	90(10)	N42	0.9167(6)	0.1928(6)	0.2951(4)	48(6)
C17	0.5795(8)	0.3711(8)	0.2236(6)	67(8)	C43	0.9176(8)	0.2931(7)	0.2397(6)	48(7)
C18	0.5078(8)	0.3744(8)	0.2904(6)	56(7)	C44	0.8554(9)	0.4008(8)	0.2350(6)	66(10)
N19	0.5164(6)	0.2908(6)	0.3724(4)	43(6)	C45	0.8746(10)	0.4833(8)	0.1708(7)	77(10)
C20	0.4996(7)	0.0814(7)	0.6042(6)	44(7)	C46	0.9546(10)	0.4583(8)	0.1133(7)	81(10)
C21	0.6036(7)	−0.0222(7)	0.6067(5)	42(7)	C47	1.0175(9)	0.3524(8)	0.1173(6)	67(10)
N22	0.6413(6)	−0.1262(6)	0.6680(4)	48(6)	C48	0.9966(8)	0.2690(7)	0.1808(5)	43(7)
C23	0.7373(8)	−0.1959(7)	0.6430(6)	46(7)	N49	1.0416(6)	0.1538(6)	0.2011(4)	42(6)
C24	0.8080(8)	−0.3117(8)	0.6813(6)	58(8)	Cl	0.1253(3)	0.6034(3)	0.39987(22)	96(3)

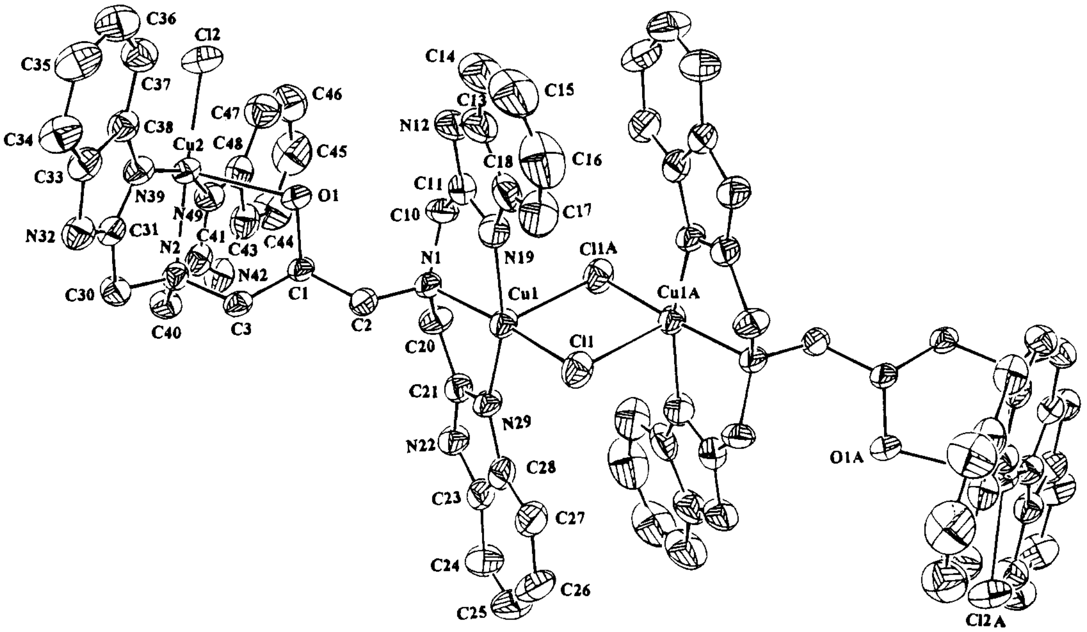

Figure 4. ORTEP drawing of Cu_2(HL-H)Cl_2(ClO_4)$_2$·1.5Et_2O·CH_3OH, **3**. For clarity, solvent molecules and hydrogen atoms are omitted.

be rationalized by invocation of a driving force for Cu(II) to be pentacoordinate. Thus in **1** and **2**, only three of four available chlorides coordinate to the copper ions whereas the fourth does not coordinate because both copper ions are already pentacoordinate. In **3**, in the absence of dimerization, Cu1 would be tetracoordinate. After dimerization, both copper ions become pentacoordinate. In **4**, the hydroxy oxygen bridges the two copper ions to achieve pentacoordination for both copper ions. The reason that **3** is a dimer whereas **4** is a monomer is unclear, but the energies of **3** and **4** must differ only slightly.

This driving force to form pentacoordinate Cu(II) may be related to the oxygen transport property of hemocyanin. The model complex reported by Takajima[37−42] and co-workers in which each copper ion is surrounded by tripodal N_3 ligand and bridged by $O_2$2- to form a μ_2-η^2:η^2-O_2 binuclear Cu(II) complex represents the most accurate model of oxyhemocyanin. Under this bonding mode of O_2, both tripodal N_3 coordinated Cu(II) complexes are pentacoordinate without participation of an additional ligand.

Coordination of copper ions with a multidentate binucleating ligand does not automatically result in pentacoordinate Cu(II). For example, when pentadentate ligands derived from 2,6-diformyl-*p*-cresol, which were pioneered by Robson and Okawa,[47,48] are used to synthesize binuclear copper(II) complexes, planar tetracoordinate Cu(II) geometries are found invariably. The NOX (O from bridging phenoxo, X = N or O) endogenous coordinating atoms in ligands of the Robson type are ideally positioned at three vertices of a square. Together with an exogenous bridging ligand, planar tetracoor-

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(48) Okawa, H.; Kida, S. *Bull. Chem. Soc. Jpn.* **1971**, *44*, 1172.

Table 6: Atomic Coordinates *x*, *y*, *z* and Equivalent Isotropic Displacement Coefficients ($Å^2 \times 10^3$) for Non-Hydrogen Atoms of the Cation of $Cu_2(HL\text{-}H)Cl_2(ClO_4)_2 \cdot 1.5Et_2O \cdot CH_3OH$, **3**

	x	*y*	*z*	U_{eq}		*x*	*y*	*z*	U_{eq}
Cu1	0.46818(12)	0.07383(10)	0.09876(8)	35(1)	C25	0.7364(16)	0.4869(11)	0.0519(10)	87(12)
Cu2	0.10812(12)	0.42256(10)	0.41082(8)	33(7)	C26	0.7893(14)	0.4077(12)	0.0087(9)	84(11)
C11	0.6551(3)	0.04406(24)	0.03542(18)	45(1)	C27	0.7196(13)	0.3106(11)	0.0277(8)	66(10)
C12	0.0604(3)	0.52062(24)	0.35155(21)	53(2)	C28	0.5912(12)	0.2983(9)	0.0517(7)	51(8)
N1	0.3007(8)	0.1122(7)	0.1697(5)	33(5)	N29	0.4948(9)	0.2132(7)	0.0771(6)	44(6)
N2	0.1599(8)	0.3297(6)	0.4630(5)	33(5)	C30	0.2170(10)	0.4049(8)	0.5341(6)	38(7)
C1	0.2289(9)	0.2361(8)	0.3134(6)	30(6)	C31	0.2793(10)	0.5114(9)	0.5124(7)	39(7)
C2	0.3278(9)	0.1788(8)	0.2528(6)	34(6)	N32	0.3735(8)	0.5883(7)	0.5446(6)	42(6)
C3	0.2538(9)	0.2752(8)	0.3989(6)	32(6)	C33	0.3992(10)	0.6742(9)	0.5109(7)	42(7)
O1	0.2259(7)	0.3281(6)	0.2917(4)	42(5)	C34	0.4892(11)	0.7734(9)	0.5210(8)	53(8)
C10	0.2054(10)	0.0060(8)	0.1728(7)	41(7)	C35	0.4922(12)	0.8400(10)	0.4764(9)	61(10)
C11	0.2761(10)	−0.0683(8)	0.1722(6)	37(7)	C36	0.4113(12)	0.8096(10)	0.4244(9)	60(10)
N12	0.2252(8)	−0.1598(7)	0.1971(6)	43(6)	C37	0.3210(11)	0.7106(9)	0.4143(7)	48(7)
C13	0.3219(11)	−0.2036(9)	0.1864(7)	42(7)	C38	0.3179(10)	0.6422(9)	0.4582(7)	39(7)
C14	0.3237(13)	−0.2931(10)	0.2070(8)	60(10)	N39	0.2409(8)	0.5369(7)	0.4606(5)	37(6)
C15	0.4367(14)	−0.3121(11)	0.1919(9)	68(11)	C40	0.0445(10)	0.2471(9)	0.4902(7)	38(7)
C16	0.5457(13)	−0.2469(10)	0.5180(9)	61(10)	C41	−0.0421(10)	0.2235(8)	0.4359(6)	38(6)
C17	0.5449(11)	−0.1568(10)	0.1385(7)	51(7)	N42	−0.1353(8)	0.1321(7)	0.4205(6)	44(6)
C18	0.4305(10)	−0.1354(8)	0.1546(6)	39(7)	C43	−0.1948(11)	0.1434(9)	0.3685(7)	48(7)
N19	0.3980(8)	−0.0501(6)	0.1451(5)	35(5)	C44	−0.2950(13)	0.0753(11)	0.3329(9)	66(10)
C20	0.2697(10)	0.1724(9)	0.1248(7)	41(7)	C(45)	−0.3306(14)	0.1110(12)	0.2838(9)	76(11)
C21	0.3925(11)	0.2433(9)	0.0957(7)	44(7)	C46	−0.2700(13)	0.2120(11)	0.2681(9)	66(10)
N22	0.4104(10)	0.3427(7)	0.0854(6)	53(7)	C47	−0.1689(12)	0.2801(10)	0.3023(8)	58(8)
C23	0.5361(13)	0.3787(10)	0.0579(7)	60(10)	C48	−0.1314(10)	0.2452(9)	0.3539(7)	39(6)
C24	0.6096(16)	0.4775(11)	0.0407(9)	77(12)	N49	−0.0361(8)	0.2938(7)	0.3977(5)	38(6)

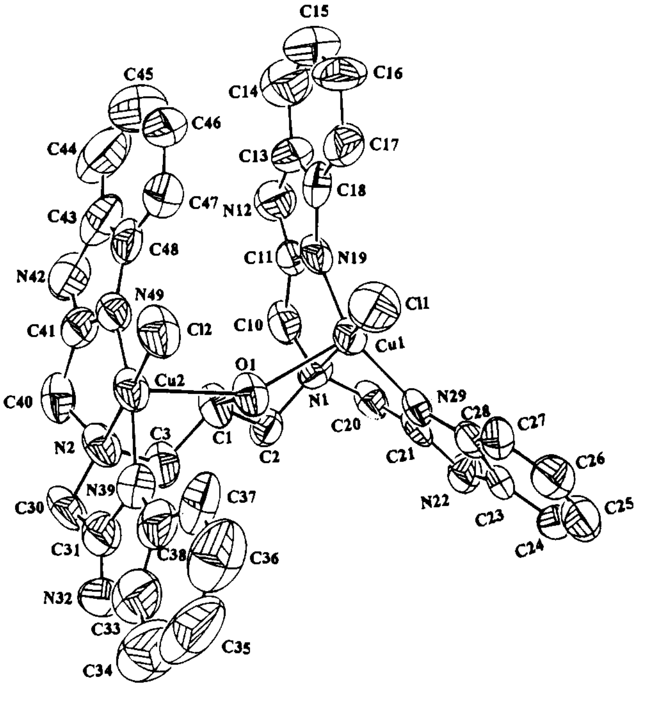

Figure 5. ORTEP drawing of $Cu_2(HL\text{-}H)Cl_2(ClO_4)_2 \cdot 5H_2O \cdot Et_2O \cdot C_2H_5OH$, **4**. For clarity, solvent molecules and hydrogen atoms are omitted.

dinate Cu(II) complexes are formed. Using propan-2-ol instead of *p*-cresol, the resulting pentadentate ligand of the Robson type also gives a tetracoordinate planar dicopper complex.[27,28] Therefore the tripodal N_3 (consisting of two aromatic nitrogen atoms N_{ar} and one amine nitrogen N_{am}) coordination site in the ligand HL-H must be special so that the coordinated copper ion is favored to form a pentacoordinate complex. In the $Cu1N_3Cl_2$ coordination geometry of **3** and the $Cu2N_3OCl$ coordination geometry of **4**, the shape-determining dihedral angles e_3 are near the value of ideal SP. Furthermore, for these two geometries the copper ions are within 0.1Å of the basal planes. If bonding with the axial ligand is neglected, tetracoordinate copper complexes can thus be formed with the tripodal N_3 ligating site. In these nearly planar geometries, the tripodal nitrogen atoms are so constrained that the copper ions cannot be located at the centers of the N_3 coordination sites as evident from data that the $N_{ar}-Cu1-N_{am}$ angles are only ca. 80°. Instead, the copper ions lean toward the fourth coordinating atoms. For this reason copper ions surrounded by the tripodal N_3 ligand may tend to form a pentacoordinate geometry.

The N_3 tripodal geometries in **1**−**4** that are in a relaxed state because there is no strain induced by any exogenous bridging ligand should be the most favorable arrangement. Particular features of these geometries are that the range of $N_{ar}-Cu-N_{ar}$ angles (including ∠N19−Cu1−N29 and ∠N39−Cu2−N49) is 146−164°, and the narrow range of $N_{am}-Cu-N_{ar}$ angles (including ∠N1−Cu1−N19, ∠N1−Cu1−N29, ∠N2−Cu2−N39, and ∠N2-Cu2-N49) is 79−84°. These $N_{ar}-Cu-N_{ar}$ angles are much larger than those reported by Reed et al.[24−26] in $[Cu_2(L\text{-}Et)(\mu\text{-}X)]^{2+}$ ($X = N_3^-$, OAc^- ,and NO_2^-) in which the $N_{ar}-Cu-N_{ar}$ angles are between 99 and 108°, whereas the $N_{am}-Cu-N_{ar}$ angles are similar to those in **1**−**4**. In contrast to complexes **1**−**4**, the ligand in $[Cu_2(L\text{-}Et)(\mu\text{-}X)]^{2+}$ ($X = N_3^-$, OAc^-, and NO_2^-) has the ethyl group bonded to the amino nitrogen. Whether these ethyl groups are responsible for the large variation in $N_{ar}-Cu-N_{ar}$ angles is uncertain. In the diiron(III) complexes, [$Fe_4O_2(L\text{-}H)_2(Obz)_2]^{4+}$ and $[Fe_4O_2(L\text{-}Et)_2(OAc)_2]$,[49] the $N_{ar}-Fe-N_{ar}$ angles lie in a narrow range 80.5−83.6°, whereas the $N_{am}-Fe-N_{ar}$ angles are between 75 and 78°. The coordination geometries of $L\text{-}H^-$ and $L\text{-}Et^-$ are similar. Therefore, the large variation of $N_{ar}-Cu-N_{ar}$ angles of **1**−**4** and the exogenous ligand bridged $[Cu_2(L\text{-}Et)(\mu\text{-}X)]^{2+}$ ($X = N_3^-$, OAc^- ,and NO_2^-) are not due to ethyl groups in $L\text{-}Et^-$. Another conspicuous distinction in complexes **1**−**4** and $[Cu_2(L\text{-}Et)(\mu\text{-}X)]^{2+}$ ($X = N_3^-$, OAc^- ,and NO_2^-), is that in the latter complexes there are both endogenous alkoxo and exogenous X bridging groups. Whether both bridging groups are required to induce the difference ca. 40° in $\angle N_{ar}-Cu-N_{ar}$ remains unclear. Structural data of phenoxo-bridged $[Cu_2(bimp)(CH_3OH)_2]^{3+}$ and $[Cu_2(bimp)(\mu\text{-}CH_3O)]^{2+}$ [23] (Hbimp is 2,6-bis[bis((1-methylimidazol-2-yl)methyl)amino]-4-methylphenol) indi-

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Table 7. Atomic Coordinates *x*, *y*, *z* and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^3) for Non-Hydrogen Atoms of the Cation of $Cu_2(HL\text{-}H)Cl_2(ClO_4)_2 \cdot 5H_2O \cdot Et_2O \cdot C_2H_5OH$, **4**

	x	y	z	U_{eq}		x	y	z	U_{eq}
Cu1	0.1948(3)	0.9250(3)	0.14731(23)	56(2)	C25	0.007(3)	1.231(3)	0.0597(22)	92(30)
Cu2	0.4826(3)	1.0175(3)	0.40681(22)	63(2)	C26	−0.019(3)	1.186(3)	0.1107(21)	84(29)
Cl1	0.0748(20)	0.9252(17)	0.1992(13)	101(18)	C27	0.032(3)	1.120(3)	0.1295(18)	66(25)
Cl2	0.3218(8)	0.9796(8)	0.4502(5)	84(7)	C28	0.111(3)	1.0939(23)	0.0922(17)	57(21)
N1	0.3400(22)	0.9357(17)	0.1064(13)	52(18)	N29	0.1756(19)	1.0301(18)	0.1003(13)	49(17)
N2	0.6430(22)	1.0560(21)	0.3705(14)	67(20)	C30	0.735(3)	1.149(3)	0.4255(18)	75(26)
C1	0.475(3)	0.997(3)	0.2405(16)	63(24)	C31	0.663(3)	1.210(3)	0.4517(19)	80(27)
C2	0.460(3)	1.0144(24)	0.1645(17)	58(24)	N32	0.701(3)	1.3058(21)	0.4843(16)	91(25)
C3	0.607(3)	1.076(3)	0.2973(18)	75(27)	C33	0.605(4)	1.327(3)	0.5027(20)	99(37)
O1	0.3699(17)	1.0102(16)	0.2629(10)	60(15)	C34	0.605(6)	1.414(4)	0.536(3)	153(58)
C10	0.359(3)	0.843(3)	0.0901(18)	70(26)	C35	0.484(7)	1.408(4)	0.546(3)	186(70)
C11	0.258(3)	0.7652(23)	0.1026(16)	54(21)	C36	0.379(5)	1.318(4)	0.523(3)	137(51)
N12	0.2403(25)	0.6675(21)	0.0828(16)	77(24)	C37	0.388(4)	1.232(3)	0.4901(21)	101(36)
C13	0.137(3)	0.628(3)	0.1046(20)	82(29)	C38	0.508(4)	1.235(3)	0.4788(18)	81(31)
C14	0.074(4)	0.523(3)	0.093(3)	117(44)	N39	0.5411(24)	1.1627(20)	0.4471(14)	70(21)
C15	−0.032(4)	0.505(3)	0.116(3)	122(41)	C40	0.685(3)	0.971(3)	0.3675(18)	71(27)
C16	−0.074(4)	0.573(3)	0.1420(24)	95(34)	C41	0.574(3)	0.879(3)	0.3501(18)	71(26)
C17	−0.011(3)	0.674(3)	0.1523(21)	81(30)	N42	0.564(3)	0.7883(23)	0.3199(17)	89(26)
C18	0.100(3)	0.698(3)	0.1316(18)	66(26)	C43	0.439(4)	0.727(3)	0.3103(22)	101(36)
N19	0.1811(20)	0.7902(20)	0.1319(13)	61(18)	C44	0.388(6)	0.623(3)	0.278(3)	146(55)
C20	0.308(3)	0.9697(24)	0.0397(16)	57(22)	C45	0.261(5)	0.586(3)	0.282(3)	152(50)
C21	0.236(3)	1.0364(23)	0.0526(16)	58(21)	C46	0.206(4)	0.642(3)	0.3068(23)	108(35)
N22	0.2176(23)	1.1033(20)	0.0156(14)	65(20)	C47	0.261(3)	0.745(3)	0.3356(21)	87(30)
C23	0.140(3)	1.1410(23)	0.0396(17)	61(22)	C48	0.386(3)	0.785(3)	0.3376(17)	71(27)
C24	0.085(3)	1.2115(25)	0.0228(20)	80(27)	N49	0.4711(22)	0.8852(19)	0.3641(13)	62(18)

cate that the $N_{am}-Cu-N_{ar}$ angles lie in the narrow range 80.4−83.5°. In contrast, the N_{ar}-Cu-N_{ar} angle altered from 150−155° for the nonexogenously bridged complex to 113.1° for the methoxide-bridged complex. These results indicate that the presence of the exogenously bridging group is the major reason for the decreased $N_{ar}-Cu-N_{ar}$ angle.

Besides the absence of the exogenously bridging group, another notable feature of **1**−**4** is that the endogenous hydroxy group coordinated to Cu(II) ions retains its hydrogen. This feature is discernible from the Cu(II)−O distances (2.30−2.72 Å), which are much greater than those (1.85−2.16 Å) found in deprotonated analogous complexes: $[Cu_2(L\text{-}Et)(\mu\text{-}X)]^{2+}$ (X = N_3−, OAc^- ,and NO_2^-).[24−26] The phenolic proton is dissociated for all reported binuclear copper(II) complexes having a bridging phenol moiety.[9−23] This effect is probably due to the acidity of the phenolic proton. The deprotonation of an aliphatic hydroxy group in a binucleating ligand can be accomplished by two methods, either by proton abstraction by a base or by the presence of an exogenous bridging ligand. Despite our attempts to extract the proton by addition of NEt_3 during the preparation of **4**, the proton remained on the hydroxyl group. The presence of an exogenously bridging ligand forces the two copper(II) ions to be near the hydroxy group so as to ensure strong interaction between copper ions and oxygen and consequently to lead to deprotonation. The energy gained from the strong Cu(II)−O interaction is obviously sufficient to offset the strain of bringing two copper ions into a bridging structure indicated by the decreased $N_{ar}-Cu-N_{ar}$ angles in $[Cu_2(L\text{-}Et)(\mu\text{-}X)]^{2+}$ (X = N_3−, OAc^-, and NO_2^-). During the preparation of **2**, the addition of the potential bridging azide resulted in a non-azide complex. A possible explanation is that to form an azide bridge it is necessary both to replace the coordinated chlorides and to bring the two copper ions together by substantially decreasing the $N_{ar}-Cu-N_{ar}$ angles; this process may be energetically unfavorable.

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Supplementary Material Available: Tables of crystallographic parameters, atomic coordinates, thermal parameters, bond distances and angles, and least-squares planes for complexes **1**−**4** (33 pages). Ordering information is given on any current masthead page.

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