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

Weng Feng Zeng,[†,‡] Cheu Pyeng Cheng,[*,†] Sung Mao Wang,[*,†] and Gene-Hsian Lee[§]

Department of Chemistry, National Tsing Hua University, Hsin-Chu, Taiwan,
Tajen Junior College of Pharmacy, Pin-Tung, Taiwan, and Department of Chemistry,
National Taiwan University, Taipei, Taiwan

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The structures of five dicopper complexes of binucleating ligand HL-H (*N*,*N*,*N*′,*N*′-tetrakis[(2-benzimidazolyl)-methyl]-2-hydroxy-1,3-diaminopropane) with thiocyanate and some other counterions were investigated by the X-ray diffraction method. In $\mathrm{Cu_2(HL\text{-}H)(NCS)_2Cl_2\cdot 6H_2O\cdot CH_3OH}$, **1** ($a = 12.524(5)$ Å, $b = 14.429(4)$ Å, $c = 16.343(3)$ Å, $\alpha = 109.01(2)°$, $\beta = 92.62(2)°$, $\gamma = 115.27(3)°$, $Z = 2$, triclinic, $P\bar{1}$), one chloride is not coordinated. Distorted square pyramidal (SP) geometry is found for both $\mathrm{CuN_3ClN}$ and $\mathrm{CuN_3ON}$ coordination sites in which the $\mathrm{N_3}$ tripodal coordination sites come from the two symmetric halves of HL-H and the other nitrogen atoms come from thiocyanate ions. In $\mathrm{Cu_2(HL\text{-}H)(NCS)_2(ClO_4)_2\cdot 6H_2O\cdot 2EtOH}$, **2** ($a = 10.955(2)$ Å, $b = 15.366(5)$ Å, $c = 18.465(9)$ Å, $\alpha = 65.57(4)°$, $\beta = 89.73(3)°$, $\gamma = 79.81(2)°$, $Z = 2$, triclinic, $P\bar{1}$), the coordination environments for the two copper ions are both $\mathrm{CuN_3ON}$. However, their geometries are different: one is distorted SP and the other is distorted trigonal bipyramid (TBP). In $\mathrm{Cu_2(HL\text{-}H)(NCS)_2(ClO_4)_2Cl\cdot H_3O\cdot 3.5H_2O}$, **3** ($a = 11.986(6)$ Å, $b = 12.778(5)$ Å, $c = 17.81(1)$ Å, $\alpha = 82.41(4)°$, $\beta = 75.44(5)°$, $\gamma = 78.46(4)°$, $Z = 2$, triclinic, $P\bar{1}$), the chloride ion does not coordinate to copper ion, but it is hydrogen bonded to the hydroxy hydrogen. The coordination environments for the two copper ions are both $\mathrm{CuN_3ON}$ with distorted SP geometries. In $\mathrm{Cu_2(HL\text{-}H)(NCS)Cl_3\cdot 6H_2O}$, **4** ($a = 12.026(5)$ Å, $b = 14.369(6)$ Å, $c = 16.430(6)$ Å, $\alpha = 111.64(3)°$, $\beta = 90.51(4)°$, $\gamma = 113.90(3)°$, $Z = 2$, triclinic, $P\bar{1}$), one chloride does not coordinate. The coordination environments for the two copper ions are $\mathrm{CuN_3ON}$ in severely distorted TBP geometry and $\mathrm{CuN_3Cl_2}$ in SP geometry. In $\mathrm{Cu_2(HL\text{-}H)(NCS)_3OH\cdot 2H_2O\cdot 3CH_3OH\cdot Et_2O}$, **5** ($a = 18.322(5)$ Å, $b = 15.543(6)$ Å, $c = 19.428(7)$ Å, $\beta = 102.78(3)°$, $Z = 4$, monoclinic, $P2_1/c$), the hydroxide ion does not coordinate. The coordination environments for the two copper ions are $\mathrm{CuN_3N_2}$ with a geometry inbetween SP and TBP but slightly closer to SP and $\mathrm{CuN_3ON}$ in distorted SP geometry. The distances between the copper ions are in the range 4.45−7.99 Å, indicating negligible interaction between the copper ions. The hydroxy groups of HL-H in **1**−**5** all coordinate to copper ions either in a terminal mode (in complexes **1**, **4**, and **5**, denoted as OHR(t)) or in a bridging mode (in complexes **2** and **3**, denoted as OHR(b)). These hydroxy groups do not lose their protons in all cases. All thiocyanate anions coordinate to copper ions through nitrogen atoms. All copper ions in **1**−**5** are pentacoordinated. The fact that the $\mathrm{CuN_3}$ geometries of the tripodal coordination sites in HL-H do not allow the formation of a square planar complex, may be the driving force for the formation of pentacoordinated complexes. From the structurally known dicopper complexes of the HL-H type ligands, the relative coordinating abilities of ligands to $\mathrm{CuN_3}$ are OHR(t) > $\mathrm{NCS^-}$ > $\mathrm{Cl^-}$(t) > OHR(b) ≈ $\mathrm{Cl^-}$(b), where the letters b and t in parentheses denote bridging and terminal coordination modes respectively.

Introduction

A large number of dicopper complexes have been studied as model compounds of hemocyanins (Hc)[1,2] which serve as $\mathrm{O_2}$ carriers for many molluscs and arthropods. Among these model compounds, the complexes of polydentate ligands with endogenous hydroxy groups have attracted considerable attention.[3−7] The dicopper complex of *N*,*N*,*N*′,*N*′-tetrakis[2-(1-ethylbenzimidazolyl)methyl]-2-hydroxy-1,3-diaminopropane (HL-Et)[3−5] with an exogenous azide bridging ligand can reproduce the properties of azido-*met*-hemocyanin in that it is nearly 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.

In spite of these similar properties to *met*-hemocyanin, no oxygen binding ability of the dicopper complexes with ligands containing endogenous hydroxy group was found. It has been established that the dicopper complexes with oxygen coordinated in a μ_2:η^2:η^2 mode[8−13] can reproduce the gross spectral features and magnetic property of oxyhemocyanin. In these excellent

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[†] National Tsing Hua University.

[‡] Tajen Junior College of Pharmacy.

[§] National Taiwan University.

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model dicopper complexes, the ligands contain tripodal nitrogen coordination site for each copper ion and no other endogenous coordinating functional group including hydroxy group. Although dicopper complexes of HL-Et or HL-H may not be good model compounds to Hc, they are of interest intrinsically. Recently, we reported the crystal structures of $Cu_2(HL\text{-}H)Cl_n^{4-n}$ ($n = 2$ and 4)[14] which show that the ligand HL-H is flexible and exhibit a variety of coordination modes in forming dicopper complexes. Extending this work, here the structures of five dicupric complexes containing thiocyanate anion(s) are reported. The coordinating ability of the endogenous hydroxy group in HL-H is accessed; these results shed light on the reason why dicopper complexes of HL-H or HL-Et do not bind to oxygen in a $\mu_2{:}\eta^2{:}\eta^2$ fashion.

Experimental Section

The reagents used in this work were GR 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, and 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 contents in complexes. ^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 susceptibilities were measured on a Quantum Design Mpms Squid magnetometer operated at either 1.0 T (for complex **2**) or 0.3 T (for complex **4**). EPR spectra were recorded on a Bruker ER-200D X-band spectrometer.

Preparation of HL-H (*N,N,N′,N′*-Tetrakis[(2-benzimidazolyl)-methyl]-2-hydroxy-1,3-diaminopropane). This potentially heptadentate ligand was prepared by the reaction between 2-hydroxy-1,3-diaminopropanetetraacetic acid and 1,2-diaminobenzene according to the literature procedure.[14,15] The off-white crude product obtained from neutralizing the 4 M HCl solution of HL-H with ammonia had HCl associated with it. It was identified by ^1H NMR and IR. This crude product denoted as HL-H·*n*HCl (based on the results of elemental analysis, $n \approx 1$), was used as starting compound for the preparation of dicopper complexes.

Preparation of $Cu_2(HL\text{-}H)(NCS)_2Cl_2$, 1. A 10 mL ethanol solution of $CuCl_2{\cdot}2H_2O$ (0.538g, 3.16 mmol.) was added slowly to a 490 mL ethanol solution of HL-H·*n*HCl (0.93g, 1.43 mmol). Formation of some solid suspension could be observed. A 300 mL methanol solution of NH_4SCN (0.245g, 3.22 mmol) was added slowly to the reaction mixture. After the mixture was stirred for 3 days, product was obtained following the workup procedure of filtration, washing with 100 mL of ethanol and drying in a 50 °C vacuum oven. Yield: 0.97 g (66% based on HL-H). Anal. Found (calcd) for $Cu_2(HL\text{-}H)(NCS)_2Cl_2{\cdot}6H_2O$ ($Cu_2C_{37}H_{46}N_{12}O_7Cl_2S_2$): Cu, 12.42 (12.30); C, 42.80(43.02); H, 4.44-(4.49); N, 15.86 (16.27); O, 10.15 (10.84); Cl, 6.42 (6.86); S: 5.92 (6.21). A single crystal was obtained by dissolving the product in methanol followed by the liquid diffusion technique using diethyl ether as diffusant.

Preparation of $Cu_2(HL\text{-}H)(NCS)_2(ClO_4)_2$, 2. At 50 °C, a 350 mL methanol solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (1.1 g, 3.0 mmol) was added slowly to a 50 mL methanol solution of HL-H·*n*HCl (0.909 g, 1.41 mmol). After 2 h of reaction time, a 10 mL methanol solution of NH_4SCN (0.223 g, 2.93 mmol) was also added. The reaction mixture was stirred constantly until the volume was reduced to 200 mL, and precipitation could be observed. Following the workup procedure of filtration, washing with 20 mL of ethanol and drying in a vacuum oven at 50 °C, a green product was obtained. Yield: 0.80 g (51% based on HL-H). Anal. Found (calcd) for $Cu_2(HL\text{-}H)(NCS)_2(ClO_4)_2{\cdot}4H_2O$ ($Cu_2C_{37}H_{42}N_{12}O_{13}Cl_2S_2$): Cu, 12.11 (11.30); C, 39.37 (39.51); H, 3.78 (3.76); N, 14.72 (14.94); O, 18.49 (18.49); Cl, 6.05 (6.30); S, 5.48 (5.70). A single crystal of **2** was grown by dissolving the product in ethanol followed by the solvent diffusion technique using diethyl ether as diffusant.

Preparation of $Cu_2(HL\text{-}H)(NCS)_2(ClO_4)_2Cl^-(H_3O)^+$, 3. A 350 mL methanol solution of $Cu(CH_3CN)_4\ ClO_4$ (0.974 g, 2.98 mmol) was bubbled with O_2 for 2 h, followed by standing in air for 3 days to oxidize all Cu(I) to Cu(II). The procedure of preparing this complex is identical with that used to prepare **2**. Yield: 0.87 g (66% based on HL-H). Anal. Found (calcd) for $Cu_2(HL\text{-}H)(NCS)_2(ClO_4)_2{\cdot}4H_2O$ ($Cu_2C_{37}H_{42}N_{12}O_{13}Cl_2S_2$): Cu, 11.30 (11.30); C, 39.41 (39.51); H, 3.86 (3.76); N, 14.95 (14.94); O, 17.98 (18.49); Cl, 6.51 (6.30); S, 5.92 (5.70). A single crystal of the product was obtained from its methanolic preparation mixture by the solvent diffusion technique using diethyl ether as diffusant.

Preparation of $Cu_2(HL\text{-}H)(NCS)Cl_3$, 4. 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 HL-H·*n*HCl (1.0 g, 1.55 mmol). After 20 min of reaction time, a methanol solution of NH_4SCN(0.126 g, 1.66 mmol) was added. After the volume of the reaction mixture was reduced to 70 mL under constant stirring, a small portion (2 mL) was used to grow a single crystal employing the solvent diffusion technique using diethyl ether as diffusant. The volume of the reaction mixture was further reduced to 50 mL; a solid precipitate could be observed. After the workup procedure of filtration, washing with 50 mL of methanol, and drying in a vacuum oven at 50 °C, a green product was obtained. Yield: 0.81 g (54% based on HL-H). Anal. Found (calcd) for $Cu_2(HL\text{-}H)(NCS)Cl_3{\cdot}4H_2O$ ($Cu_2C_{36}H_{42}N_{11}O_5Cl_3S$): Cu, 12.93 (13.04); C, 44.31 (44.38); H, 4.35 (4.34); N, 15.95 (15.81); O, 8.40 (8.21); Cl, 10.94 (10.92); S, 3.18 (3.29).

Preparation of $Cu_2(HL\text{-}H)\ (NCS)_3(OH)$, 5, and $Cu_2(HL\text{-}H)(NCS)_3(ClO_4){\cdot}4H_2O$. The procedure of preparing **5** is the same as that used to prepare **3** with the modification of using twice amount of NH_4SCN (0.455 g, 5.98 mmol). A single crystal of **5** was obtained by dissolving the product in methanol followed by the solvent diffusion method using diethyl ether as diffusant. The product was further purified by recrystallization from ethanol and being dried in a vacuum oven at 50 °C. Yield: 0.86 g (56% based on HL-H). Anal. Found (calcd) for $Cu_2(HL\text{-}H)\ (NCS)_3(ClO_4){\cdot}4H_2O$ ($Cu_2C_{38}H_{42}N_{13}O_9ClS_3$): Cu, 12.51 (11.73); C, 41.36 (42.12); H, 4.05 (3.91); N, 16.72 (16.80); O, 12.75 (13.29); Cl, 3.11 (3.27); S, 8.84 (8.88).

Magnetic susceptibilities of **2** and **4** (the samples used in elemental analysis) in the temperature range of 3−300 K (see Supporting Information) were measured by a SQUID magnetometer and analyzed according to eq 1,[15,16] where *p* is the percentage of mononuclear copper

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

complex and TIP is the temperature independent paramagnetism. The results of the nonlinear least square fitting yielded the following parameters: $p = 0$, $J = -0.384(7)\ \mathrm{cm}^{-1}$, $g = 1.994(2)$, and $\chi_0 + \mathrm{TIP} = -8.4(4) \times 10^{-4}$ for **2**; $p = 0$, $J = -0.36(1)\ \mathrm{cm}^{-1}$, $g = 2.000(3)$, and $\chi_0 + \mathrm{TIP} = -6.2(5) \times 10^{-4}$ for **4**.

In pure solid powder, the EPR spectrum of each complex of **1**−**5** consists of a broad single peak. To reduce the line width, the spectrum of each complex in DMSO solution at 298 and 77 K were measured. However, the spectral line width for each complex is still broad. The *g* values are $g_{\parallel} = 2.28$ and $g_{\perp} = 2.08$; they are the same for **1**−**5**.

X-ray Crystallography. Single crystals of **1**−**5** were each sealed in epoxy resin to prevent loss of coordinating solvents that led to

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Table 1. Summary of Crystal Data and Intensity Collection Conditions of Single Crystals **1**−**5**

	1	**2**	**3**	**4**	**5**
formula	$Cu_2C_{38}H_{50}N_{12}O_8Cl_2S_2$	$Cu_2C_{41}H_{58}N_{12}O_{17}Cl_2S_2$	$Cu_2C_{37}H_{44}N_{12}O_{13.5}Cl_3S_2$	$Cu_2C_{36}H_{46}N_{11}O_7Cl_3S$	$Cu_2C_{45}H_{61}N_{13}O_8S_3$
a, Å	12.524(5)	10.955(2)	11.986(6)	12.026(5)	18.322(5)
b, Å	14.429(4)	15.366(5)	12.778(5)	14.369(6)	15.543(6)
c, Å	16.343(3)	18.465(9)	17.81(1)	16.430(6)	19.428(7)
α, deg	109.01(2)	65.57(4)	82.41(4)	111.64(3)	90
β, deg	92.62(2)	89.73(3)	75.44(5)	90.51(4)	102.78(3)
γ, deg	115.27(3)	79.81(2)	78.46(4)	113.90(3)	90
V, Å^3	2466(1)	2777(2)	2577(2)	2371(2)	5396(3)
Z	2	2	2	2	4
fw	1065	1198.04	1137.32	1002.21	1132.31
space group	$P\bar{1}$ (No. 1)	$P\bar{1}$ (No. 1)	$P\bar{1}$ (No. 1)	$P\bar{1}$ (No. 1)	$P2_1/c$ (No. 14)
T, °C	25	25	25	25	25
λ, Å	0.709 30	0.709 30	0.709 30	0.709 30	0.709 30
ρ_{calc}, g cm^{-3}	1.435	1.433	1.466	1.404	1.394
μ (cm^{-1})	10.9	10.0	10.6	10.9	9.6
$R(F_o)$, %[a]	6.2	9.3	9.5	10.3	8.8
$R_w(F_o)$, %[a]	6.2	10.9	10.7	10.9	10.5

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

breakdown of the crystals. Diffraction intensity data were collected on an Enraf-Nonius CAD-4 four-circle diffractometer using monochromatic Mo Kα radiation (0.709 30 Å) from a graphite single crystal at 25 °C. The general data collection conditions 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 methods. All hydrogen atoms were placed in ideal positions in structure factor calculations. R and R_w 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

Dicopper complexes **1**, **2**, and **4** of the potentially heptadentate ligand HL-H were obtained by the simple reaction between copper salts and the ligand with different proportions of NH_4SCN to vary the coordination environments of the metal ions. In dicopper complexes **3** and **5**, Cu(II) ions were obtained from the oxidation of Cu(I) ions. Single crystals of these dicopper complexes were then obtained from their methanol or ethanol solutions by the solvent diffusion technique using diethyl ether as diffusant. The procedures of preparing these complexes and the compositions of the five single crystals are summarized in eqs 2−6.

$$2CuCl_2 + \text{HL-H}\cdot n\text{HCl} + 2SCN^- \rightarrow \underset{\mathbf{1}}{Cu_2(\text{HL-H})(NCS)_2Cl_2\cdot 6H_2O\cdot CH_3OH} \quad (2)$$

$$2Cu(ClO_4)_2 + \text{HL-H}\cdot n\text{HCl} + 2SCN^- \rightarrow \underset{\mathbf{2}}{Cu_2(\text{HL-H})(NCS)_2(ClO_4)_2\cdot 6H_2O\cdot 2EtOH} \quad (3)$$

$$2Cu(CH_3CN)_4ClO_4 + O_2 + \text{HL-H}\cdot n\text{HCl} + 2SCN^- \rightarrow \underset{\mathbf{3}}{Cu_2(\text{HL-H})(NCS)_2(ClO_4)_2Cl\cdot H_3O\cdot 3.5H_2O} \quad (4)$$

$$2CuCl_2 + \text{HL-H}\cdot n\text{HCl} + SCN^- \rightarrow \underset{\mathbf{4}}{Cu_2(\text{HL-H})(NCS)Cl_3\cdot 6H_2O} \quad (5)$$

$$2Cu(CH_3CN)_4ClO_4 + O_2 + \text{HL-H}\cdot n\text{HCl} + 4SCN^- \rightarrow \underset{\mathbf{5}}{Cu_2(\text{HL-H})(NCS)_3OH\cdot 2H_2O\cdot 3CH_3OH\cdot Et_2O} + Cu_2(\text{HL-H})(NCS)_3(ClO_4)\cdot 4H_2O \quad (6)$$

The number of thiocyanate anions in these single crystals ranges from 1 to 3 depending on the amount of thiocyanate used in preparation.

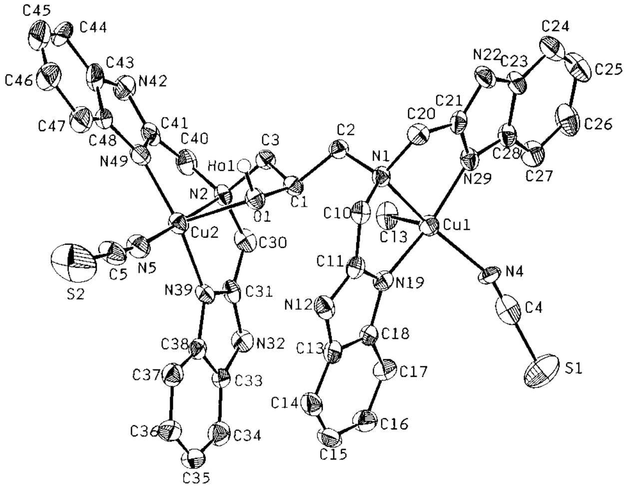

Figure 1. ORTEP drawing of $Cu_2(\text{HL-H})(NCS)_2Cl_2\cdot 6H_2O\cdot CH_3OH$, **1**. For clarity, solvent molecules and hydrogen atoms are omitted.

The results of elemental analysis of **3** indicate that the chloride ion (which is not coordinating, *vida infra*) was lost in the final workup procedure. After purification of the product from which the single crystal of **5** was obtained, $Cu_2(\text{HL-H})(NCS)_3(ClO_4)\cdot 4H_2O$ was obtained based on the results of elemental analysis. It is likely that **5** is a minor product with a good crystal growing habit, and $Cu_2(\text{HL-H})(NCS)_3(ClO_4)\cdot 4H_2O$ is the major product. It should be pointed out that both **5** and $Cu_2(\text{HL-H})(NCS)_3(ClO_4)\cdot 4H_2O$ have only three coordinated thiocyanate ions. The coordination environments for the copper ions should be roughly the same since ClO_4^- and OH^- (*vida infra*) are not coordinating.

The results of the X-ray structural determination reveal that all Cu(II) ions in these five dicopper complexes **1**−**5** are pentacoordinated. To determine whether the geometry is square pyramidal (SP) or trigonal bipyramidal (TBP), the approach of Guggenheim and Mutterties[17] which compares the actual geometry to the ideal geometries by way of a key shape determining dihedral angle e_3 was employed. This e_3 angle is 0° for SP and 53.1° for TBP.

Structure of $Cu_2(\text{HL-H})(NCS)_2Cl_2\cdot 6H_2O\cdot CH_3OH$, 1. The structure of this dithiocyanate-dichloride complex is shown in Figure 1. Atomic coordinates of significant atoms are given in Table 2; selected bond distances and bond angles are given in

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Table 2. Atomic Coordinates *x*, *y*, *z* and Equivalent Isotropic Displacement Coefficients (Å^2 × 10^{-3}) of the Significant Atoms in the Following Compounds[a]

	x	*y*	*z*	U_{eq}		*x*	*y*	*z*	U_{eq}
			(A) Cu$_2$(HL-H)(NCS)$_2$C1$_2$·6H$_2$O·CH$_3$OH, **1**						
Cu1	0.61617(11)	0.36664(11)	0.44715(8)	45(1)	C3	1.1990(8)	0.6643(8)	0.3236(6)	42(7)
Cu2	1.12179(12)	0.47101(11)	0.15854(8)	47(1)	N4	0.6396(7)	0.4164(6)	0.3444(5)	53
Cl3	0.80616(24)	0.35176(24)	0.46415(17)	59(2)	C4	0.6651(9)	0.4680(9)	0.3136(7)	66(10)
S1	0.7120(4)	0.5596(4)	0.2571(3)	113(5)	N5	1.1652(8)	0.3835(7)	0.0611(5)	61(7)
S2	1.2298(5)	0.2866(4)	−0.0864(3)	180(6)	C5	1.1922(10)	0.3449(9)	0.0022(7)	70(10)
O1	0.6981(5)	0.4412(5)	0.7414(4)	46(5)	N19	0.6652(7)	0.5109(6)	0.5385(5)	44(6)
C1	0.7150(8)	0.3803(8)	0.6593(6)	42(7)	N29	0.5143(7)	0.2100(6)	0.3775(5)	47(6)
N1	0.5237(7)	0.3170(6)	0.5467(5)	42(6)	N39	1.0376(7)	0.3593(6)	0.2087(5)	42(6)
C2	0.5940(8)	0.2846(8)	0.5969(6)	43(7)	N49	1.1274(7)	0.5815(6)	0.1093(5)	51(6)
N2	1.0832(7)	0.5723(6)	0.2654(5)	42(6)					
			(B) Cu$_2$(HL-H)(NCS)$_2$(ClO$_4$)$_2$·6H$_2$O·2EtOH, **2**						
Cu1	−0.57919(24)	0.38403(23)	−0.34572(18)	84(2)	C2	−0.8274(22)	0.424(3)	−0.2975(18)	180(40)
Cu2	−0.61776(21)	0.54621(19)	−0.19251(15)	63(1)	C3	−0.8388(18)	0.4558(20)	−0.1805(14)	98(22)
S1	−0.1490(8)	0.3305(13)	−0.3123(8)	258(17)	C4	−0.303(3)	0.3497(23)	−0.3154(19)	143(31)
S2	−0.2058(8)	0.5655(9)	−0.2132(7)	196(12)	C5	−0.3481(18)	0.5471(17)	−0.2125(12)	82(18)
O1	−0.6452(11)	0.4232(10)	−0.2355(8)	73(10)	N19	−0.5979(15)	0.2493(15)	−0.3035(11)	96(16)
N1	−0.8083(13)	0.5419(12)	−0.1717(9)	67(12)	N29	−0.6025(15)	0.5195(14)	−0.4221(10)	90(15)
N4	−0.4060(17)	0.3609(15)	−0.3221(13)	111(18)	N39	−0.5959(13)	0.4596(10)	−0.0777(8)	53(10)
N5	−0.4480(14)	0.5431(13)	−0.2132(10)	77(15)	N49	−0.6910(15)	0.6757(12)	−0.2739(9)	75(12)
C1	−0.7742(22)	0.440(3)	−0.2496(18)	148(34)					
			(C) Cu$_2$(HL-H)(NCS)$_2$(ClO$_4$)Cl·H$_3$O·3.5H$_2$O, **3**						
Cu1	0.6739(4)	0.4235(4)	0.3878(3)	64(3)	C2	0.907(3)	0.461(3)	0.3901(20)	58(2)
Cu2	0.9354(5)	0.4302(4)	0.1379(3)	75(3)	C1	0.934(3)	0.428(3)	0.3093(21)	65(2)
S1	0.3604(14)	0.4653(19)	0.2731(11)	187(2)	C3	1.042(3)	0.472(4)	0.3879(17)	71(2)
S2	0.609(3)	0.4461(23)	0.0402(17)	118(8)	N29	0.625(3)	0.562(3)	0.4350(16)	70(2)
S2′	0.598(7)	0.402(6)	0.068(4)	158(2)	N39	0.971(3)	0.283(3)	0.1620(18)	90(2)
S2″	0.552(3)	0.440(3)	0.082(3)	132(4)	N49	0.962(3)	0.573(3)	0.0933(18)	80(2)
N5	0.802(3)	0.432(3)	0.1026(21)	111(3)	Cl	0.791(3)	0.6740(23)	0.2639(18)	299(3)
O1	0.8356(19)	0.4587(19)	0.2747(13)	66(1)	H01	0.835	0.516	0.275	63
N1	0.8106(24)	0.4138(25)	0.4433(15)	66(2)					
			(D) Cu$_2$(HL-H)(NCS)Cl$_3$·6H$_2$O, **4**						
Cu1	0.6233(3)	0.8645(3)	0.44628(21)	47(2)	C2	0.5954(22)	0.7889(21)	0.6000(15)	44(2)
Cu2	0.8659(3)	1.0377(3)	0.84461(23)	65(3)	C3	0.7929(23)	0.8420(19)	0.6799(15)	56(2)
Cl3	0.8120(6)	0.8400(6)	0.4678(4)	61(6)	C1	0.7101(20)	0.8863(20)	0.6615(15)	41(2)
Cl1	0.6652(7)	0.9208(7)	0.3309(5)	81(7)	O1	0.6833(15)	0.9445(14)	0.7442(10)	57(1)
S2	0.6509(18)	1.2191(17)	1.0258(13)	104(6)	N19	0.5169(18)	0.7094(17)	0.3705(13)	53(6)
C5	0.741(5)	1.163(4)	0.974(3)	51(1)	N29	0.6692(17)	1.0089(16)	0.5412(12)	42(5)
N5	0.8051(18)	1.1319(16)	0.9477(12)	52(1)	N39	0.8650(20)	0.9335(18)	0.8963(14)	68(7)
N1	0.5210(17)	0.8188(16)	0.5463(12)	42(1)	N49	0.9531(18)	1.1462(17)	0.7966(13)	51(6)
N2	0.9128(17)	0.9320(16)	0.7428(13)	57(1)					
			(E) Cu$_2$(HL-H)(NCS)$_3$OH·2H$_2$O·3CH$_3$OH·Et$_2$O, **5**						
Cu1	0.94680(13)	0.72630(16)	0.15311(12)	46(1)	N6	0.9097(10)	0.7314(11)	0.0448(8)	70(12)
Cu2	0.63343(15)	0.52522(19)	0.05533(14)	62(16)	C1	0.7481(11)	0.6645(14)	0.0980(10)	57(13)
S1	1.2074(4)	0.7197(7)	0.2444(5)	137(7)	C2	0.7779(10)	0.7413(12)	0.1430(10)	51(12)
S2	0.5865(6)	0.3204(8)	0.2149(6)	182(10)	C3	0.6914(11)	0.6978(13)	0.0350(10)	57(12)
S3	0.8281(4)	0.7770(5)	-0.0872(3)	95(5)	C4	1.1177(11)	0.7244(17)	0.2055(11)	76(16)
O5	0.6009(13)	0.3876(16)	0.1568(12)	82(16)	C6	0.8740(12)	0.7513(11)	-0.0102(11)	61(15)
O1	0.7128(8)	0.6028(9)	0.1353(7)	71(10)	N19	0.9378(8)	0.8496(9)	0.1697(8)	48(10)
N1	0.8474(7)	0.7278(11)	0.2003(7)	48(10)	N29	0.9350(8)	0.6007(9)	0.1659(7)	44(8)
N2	0.6542(10)	0.6259(10)	-0.0101(8)	61(11)	N39	0.5425(10)	0.5909(12)	0.0512(9)	76(12)
N4	1.0579(9)	0.7238(11)	0.1804(9)	67(12)	N49	0.7143(9)	0.4663(11)	0.0216(8)	63(11)
N5	0.6124(10)	0.4339(12)	.1167(10)	82(13)					

[a] The estimated standard deviations of the least significant digits are given in parentheses. U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Tables 3 and 4. The shape-determining dihedral angles e_3 are also included in Table 3. From Figure 1, it's clear that one chloride does not coordinate to copper ion. Cu1 is surrounded by three nitrogen atoms from HL-H, one chloride and one nitrogen atom of thiocyanate ion. ∠Cu1−N4−C4 158° indicates this thiocyanate is bent. Taking Cl3 to be in the axial position, the e_3 dihedral angle between the N1−N4−N19 and N1−N4−N29 planes is 11.2°. Therefore Cu1 is in a distorted SP coordination environment. Cu1 is 0.3 Å above the least square basal plane formed by N1−N19−N4−N29. The metal ion is not located above the center of basal plane since ∠N1−Cu1−N19 and ∠N1−Cu1−N29 (80°) are much smaller than ∠N4−Cu1−N19 and ∠N4−Cu1−N29 (97°).

Cu2 is surrounded by three nitrogen atoms and one oxygen atom from HL-H as well as one nitrogen atom from thiocyanate. The thiocyanate is coordinated in a nearly linear fashion (∠Cu2−N5−C5: 171°). Considering O1 to be in the axial position, the dihedral angle e_3 between the N2−N5−N39 and N2−N5−N49 planes is 25.7° which is in between those of SP and TBP geometries but slightly closer to that of SP. It indicates that Cu2 can be assigned to a severely distorted SP geometry. As in Cu1, the angles between the basal atoms of N39−N2−N49−N5 indicates Cu2 is off the center of the basal plane and leaning toward N5. The Cu2−O1 distance (2.290 Å) is long compared with those found in Cu(II)−alkoxide or Cu(II)−phenoxide complexes.[3,5,15,18−29] It is a clear indication that the

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Table 3. Selected Bond Distances (Å) and the Shape-Determining Dihedral Angles e_3 (deg) of Complexes **1**−**5**

	1		**2**		**3**		**4**		**5**	
formula	$Cu_2(HL\text{-}H)(NCS)_2Cl_2$		$Cu_2(HL\text{-}H)(NCS)_2(ClO_4)_2$		$Cu_2(HL\text{-}H)(NCS)_2(ClO_4)_2Cl^-H_3O^+$		$Cu_2(HL\text{-}H)(NCS)Cl_3$		$Cu_2(HL\text{-}H)(NCS)_3(OH)$	
coord site	N_4Cl	N_4O	N_4O	N_4O	N_4O	N_4O	N_3Cl_2	N_4O	N_5	N_4O
Cu1−N1	2.174(7)		2.12(2)		2.09(3)		2.20(2)		2.21(1)	
Cu2−N2		2.106(8)		2.13(1)		2.08(3)		2.06(2)		2.10(2)
Cu1−N19	1.933(8)		1.94(2)		1.90(3)		1.94(2)		1.96(2)	
Cu1−N29	1.939(8)		1.94(2)		1.97(3)		1.93(2)		1.99(1)	
Cu2−N39		1.968(7)		1.97(2)		1.86(3)		1.976(2)		1.94(2)
Cu2−N49		1.984(8)		1.96(2)		1.94(3)		1.94(2)		1.97(2)
Cu1−N4[a]	2.018(7)		1.89(2)		1.93(3)		2.306(9)		1.99(2)	
Cu2−N5		1.945(8)		1.89(2)		1.86(3)		2.09(2)		1.95(2)
Cu1−Cl3[b]	2.490(3)		2.42(1)		2.48(2)		2.474(8)		2.07(2)	
Cu2−O1		2.290(6)		2.40(1)		2.47(2)		2.30(2)		2.23(1)
Cu1−Cu2	7.989(3)		4.454(4)		4.756(8)		6.269(2)		6.443(4)	
N4−C4	0.98(1)		1.11(3)		1.15(5)				1.10(3)	
C4−S1	1.77(1)		1.66(3)		1.56(4)				1.65(2)	
N5−C5		1.09(1)		1.11(3)		1.07(6)		1.06(5)		1.11(3)
C5−S2		1.62(1)		1.63(2)		1.71(5)		1.66(5)		1.60(2)
N6−C6									1.16(3)	
C6−S3									1.60(2)	
e_3[c]	11.2(5)	25.7(6)	20(1)	33.3(9)	22(2)	19(2)	9(1)	29(1)	25.9(8)	15.9(9)
d[d]	0.334(5)	0.192(5)	0.12(1)		0.14(2)	0.13(2)	0.37(1)		0.445(8)	0.13(1)

[a] The label of N4 should change to Cl1 for **4**. [b] The Cl3 labeling should be changed to O1 for **2** and **3** and to N6 for **5**. [c] The shape determining dihedral angles are between the N1−N4−N19 and N1−N4−N29 planes (**1**, **2**, **3**, and **5**) or between the N1−Cl1−N19 and N1−Cl1−N29 planes (**4**) and between N2−N5−N39 and N2−N5−N49 planes. [d] The distance between copper ions and the least-squares plane passing the four basal coordinating atoms.

Table 4. Selected Bond Angles (deg) of Compounds **1**−**5**

	1		**2**		**3**		**4**		**5**	
formula	$Cu_2(HL\text{-}H)(NCS)_2Cl_2$		$Cu_2(HL\text{-}H)(NCS)_2(ClO_4)_2$		$Cu_2(HL\text{-}H)(NCS)_2(ClO_4)_2Cl^-H_3O^+$		$Cu_2(HL\text{-}H)(NCS)Cl_3$		$Cu_2(HL\text{-}H)(NCS)_3(OH)$	
coord site	N_4Cl	N_4O	N_4O	N_4O	N_4O	N_4O	N_3Cl_2	N_4O	N_5	N_4O
N1−Cu1−N19	80.1(3)		81.7(7)		83(1)		82.0(8)		79.3(6)	
N1−Cu1−N29	80.4(3)		83.1(7)		81(1)		78.7(7)		80.5(6)	
N1−Cu1−N4[a]	156.6(3)		176.4(8)		177(1)		158.3(6)		141.1(6)	
N1−Cu1−Cl3[b]	106.2(2)		78.9(5)		79.2(9)		103.7(5)		107.9(6)	
N2−Cu2−N39		82.5(3)		81.8(6)		84(1)		79.6(9)		81.5(7)
N2−Cu2−N49		81.4(3)		81.5(7)		83(1)		84.7(8)		84.0(7)
N2−Cu2−N5		177.2(3)		176.1(7)		178(2)		174.8(7)		178.6(7)
N2−Cu2−O1		80.1(3)		80.1(5)		81(1)		81.0(7)		80.9(5)
N19−Cu1−N29	157.8(3)		156.9(7)		155(1)		156.9(7)		157.9(6)	
N39−Cu2−N49		151.4(3)		145.8(6)		158(2)		150.0(9)		158.7(7)
N19−Cu1−N4[a]	96.8(3)		97.5(8)		99(1)		95.3(6)		95.4(7)	
N19−Cu1−Cl3[b]	100.6(2)		100.1(6)		92(1)		96.4(6)		96.3(7)	
N29−Cu1−N4[a]	96.8(3)		98.7(8)		98(1)		97.9(6)		94.7(7)	
Cu1−N4−C4	158.0(9)		174(2)		172(3)				169(2)	
N4−C4−S1	179(1)		174(3)		176(4)				177(3)	
Cu1−N6−C6									160(2)	
N6−C6−S3									177(2)	
N29−Cu1−Cl3[b]	95.1(3)		93.9(6)		103(1)		100.4(6)		98.3(6)	
N4−Cu1−Cl3[a,b]	97.2(3)		97.8(7)		98(1)		98.0(3)		111.1(7)	
N39−Cu2−N5		99.5(3)		98.5(6)		98(2)		97.0(9)		97.2(8)
N49−Cu2−N5		97.5(3)		100.1(7)		97(1)		100.0(8)		97.5(8)
N39−Cu2−O1		95.6(3)		95.8(5)		92(1)		105.2(8)		99.5(7)
N49−Cu2−O1		104.7(3)		110.4(6)		103(1)		97.4(7)		93.4(6)
N5−Cu2−O1		97.8(3)		96.0(6)		97(1)		96.1(7)		98.9(6)
Cu2−N5−C5		170.6(9)		165(2)		175(5)		153(3)		173(2)
C1−O1−Cu1					101(2)					
C1−O1−Cu2						99(2)				
Cu1−O1−Cu2	131.1(2)		135.1(6)		148(1)		128.7(6)		136.4(5)	

[a] The N4 labeling should be changed to Cl1 for **4**. [b] The Cl3 labeling should be changed to O1 for **2** and **3** and to N6 for **5**.

endogenous hydroxy group does not deprotonate when coordinated to Cu2. The uncoordinated chloride anion (not shown in Figure 1) is located 3.112(8) Å away from N22. Obviously, there is a hydrogen bond between the uncoordinated chloride and amino hydrogen of N22 in a benzimidazolyl group.

An intriguing question is why the two thiocyanate anions coordinate to two Cu(II) ions separately instead of to only one copper ion. A plausible explanation will be presented, after comparing the structures of all complexes containing thiocyanate anion(s) in this work.

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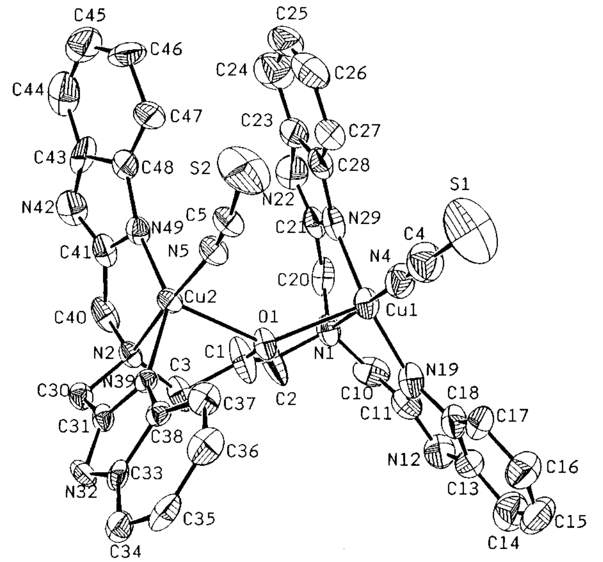


Figure 2. ORTEP drawing of $Cu_2(HL\text{-}H)(NCS)_2(ClO_4)_2{\cdot}6H_2O{\cdot}2EtOH$, **2**. For clarity, solvent molecules and hydrogen atoms are omitted.

Structure of $Cu_2(HL\text{-}H)(NCS)_2(ClO_4)_2{\cdot}6H_2O{\cdot}2EtOH$, 2. The structure of this dithiocyanate-diperchlorate dicopper complex is shown in Figure 2. Atomic coordinates of significant atoms are given in Table 2. Selected bond distances, e_3, and bond angles are given in Tables 3 and 4. The two perchlorate anions do not coordinate to any Cu(II) ion as expected. Each copper ion is coordinated by three nitrogen atoms from HL-H, one oxygen and one thiocyanate. The thiocyanate coordinated to Cu2 is markedly off linearity (∠Cu2−N5−C5 is 165°). The e_3 angle for Cu1 between the N1−N4−N19 and N1−N4−N29 planes is 20°; Cu1 is in a severely distorted SP coordination environment. The e_3 angle for Cu2 between the N2−N5−N39 and N2−N5−N49 planes is 33.3° which is closer to that of TBP. Thus, Cu2 is in a severely distorted TBP geometry. Since ∠N2−Cu2−N5 is 176°, N2 and N5 are assigned to be in the axial positions and O1, N39, and N49 are in the equatorial positions. The distortion is obvious from the angles in the equatorial plane (∠N39−Cu2−N49 = 146°, ∠N39−Cu2−O1 = 96°, and ∠N49−Cu2−O1 = 110°). If one considers the coordination geometry of Cu1 to be the same as that of Cu2, then the distortion in the basal plane is even more severe than that in Cu2 since the angles between the basal atoms are far away from the ideal 120° (∠N19−Cu1−N29 = 157°, ∠N19−Cu1−O1 = 100° and ∠N29−Cu1−O1 = 94°). Therefore, assignment of two different coordination geometries to Cu1 and Cu2 are justified despite the fact that the two copper ions are surrounded by the same coordination atoms. The endogenous hydroxy group bridges the two copper ions. Whether the hydrogen of the hydroxy group is dissociated or not cannot be detected directly by the X-ray structural determination. The Cu−O distances of 2.42 and 2.40 Å are much longer than those detected in $Cu_2(L\text{-}Et)(\mu\text{-}X)^{2+}$ ($X = N_3^-$, OAc^-, and NO_2^-)[3−5] where the hydrogen atoms of the hydroxy groups are dissociated. Therefore, it is concluded that the hydroxy group does not deprotonate to form an alkoxy group. There is only one other example (in $Cu_2(HL\text{-}H)Cl_2(ClO_4)_2$) of nondeprotonated alcoholic hydroxy group bridging between two copper ions reported previously.[14]

Structure of $Cu_2(HL\text{-}H)(NCS)_2(ClO_4)_2Cl{\cdot}H_3O{\cdot}3.5H_2O$, 3. The structure of this dithiocyanate-diperchlorate complex is shown in Figure 3. Atomic coordinates of significant atoms are given in Table 2. Selected bond distances, e_3, and bond angles are given in Tables 3 and 4. S2 is disordered. The structure of **3** is very similar to that of **2** as expected because the method of preparing **3** is almost identical to that for **2** with the minor difference that the source of copper ions for **3** is obtained from aerobic oxidation of $Cu(CH_3CN)_4ClO_4$ while $Cu(ClO_4)_2$ was used directly in the preparation of **2**.

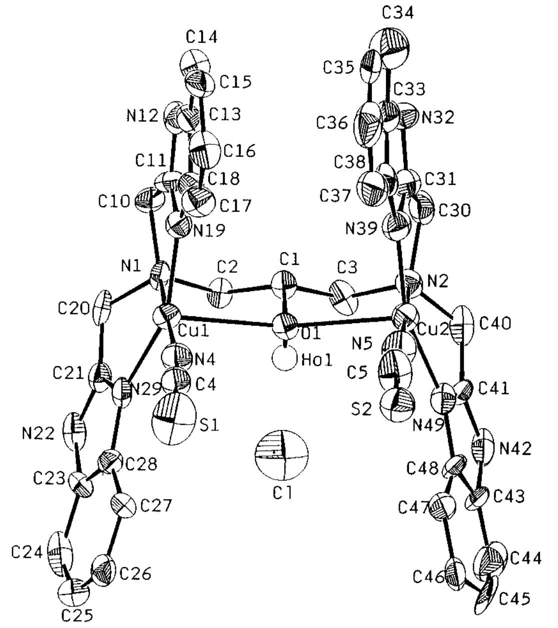


Figure 3. ORTEP drawing of $Cu_2(HL\text{-}H)(NCS)_2(ClO_4)_2Cl{\cdot}H_3O{\cdot}3.5H_2O$, **3**. For clarity, solvent molecules and hydrogen atoms are omitted.

As in **2**, both copper ions are pentacoordinated by three nitrogen atoms from HL-H, one oxygen and one thiocyanate. However, e_3 angles for the two copper ions are very close to each other with a value of ca. 20°, which is indicative of a severely distorted SP geometry.

The two perchlorate anions do not coordinate to any copper ion as in **2**. The Cu−O distance of 2.47−2.48 Å is about the same as that in **2**. However, there is an extra chloride ion which is 2.69(4) Å away from the endogenous hydroxy oxygen. It is obvious that there is a reasonable strong hydrogen bond between the hydroxy hydrogen and the chloride ion. The C1−O1−Cu1 and C1−O1−Cu2 angles are 101(2) and 99(2)° respectively. This is a rare example where the geometry of a four-bonded oxygen can be accessed by making the reasonable assumption that the hydrogen bond O1−H−Cl is linear. Then the other four angles around this tetracoordinated oxygen are Cu1−O1−Cl = 99(1)°, Cu2−O1−Cl = 99(1)°, Cu1−O1−Cu2 = 148(1)°, and C1−O1−Cl = 106(2)°. The Cu1−O1−Cu2 angle is 13° greater than the corresponding angle in **2**. It is also the greatest among **1**−**5**.

Structure of $Cu_2(HL\text{-}H)(NCS)Cl_3{\cdot}6H_2O$, 4. The structure of this monothiocyanatotrichloro complex is shown in Figure 4. The atomic coordinates of significant atoms are given in Table 2. Selected bond distances, e_3, and bond angles are given in Tables 3 and 4. Cu1 is surrounded by three nitrogen atoms and two chloride ions. It is in a slightly distorted SP geometry since e_3 between the N1−Cl1−N19 and N1−Cl1−N29 planes is 9°. Cu2 is surrounded by three nitrogen atoms, one oxygen atom, and one thiocyanate. The thiocyanate coordinates to Cu2 in a nonlinear fashion since ∠Cu2−N5−C5 is 153° which is significantly far away from 180°. The e_3 dihedral angle between N2−N5−N39 and N2−N5−N49 is 29°, which is closer to that of the TBP geometry. Therefore, Cu2 is in a severely distorted TBP geometry where N2−N5 are in the axial positions and N39, O1, and N49 are in the equatorial positions. One of the chlorides does not coordinate to any copper ion. This chloride (not shown in Figure 4) is located 3.06 Å away from the amino

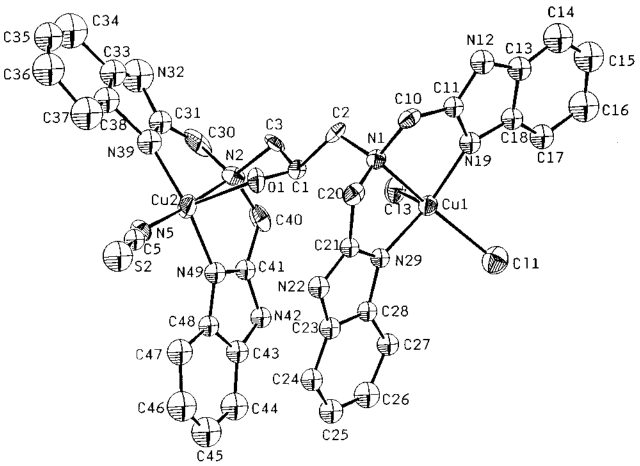


Figure 4. ORTEP drawing of Cu_2(HL-H)(NCS)Cl_3·6H_2O, **4**. For clarity, solvent molecules and hydrogen atoms are omitted.

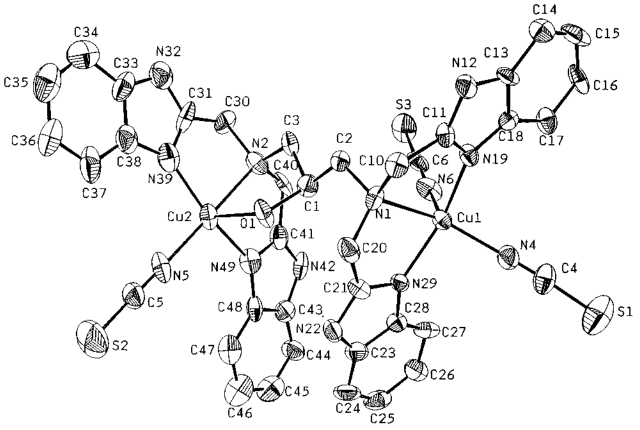


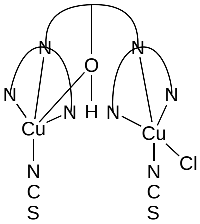
Figure 5. ORTEP drawing of Cu_2(HL-H)$(NCS)_3$OH·2H_2O·3CH_3OH·Et_2O, **5**. For clarity, solvent molecules and hydrogen atoms are omitted.

nitrogen N12 of the benzimidazolyl group, indicating the presence of a hydrogen bond. It is interesting to note that Cl1 and Cl3 coordinate to the same copper ion instead of one chloride to each copper ion.

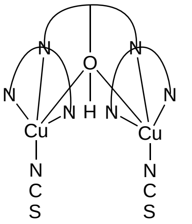
Structure of Cu_2(HL-H)$(NCS)_3$(OH)·2H_2O·3CH_3OH·Et_2O, 5. The structure of this trithiocyanate complex is shown in Figure 5. The atomic coordinates of significant atoms are given in Table 2. Selected bond distances, e_3 and bond angles are given in Tables 3 and 4. Cu1 is coordinated by three nitrogen atoms and two thiocyanate anions. The e_3 dihedral angle between the N1−N4−N19 and N1−N4−N29 planes is 25.9° which is midway between ideal SP and TBP. The coordination geometry of Cu1 can be considered either as distorted SP or distorted TBP geometries. The two thiocyanate anions coordinate slightly nonlinearly to Cu1 as judged from ∠Cu1−N4−C4 and ∠ Cu1−N6−C6 to be 169 and 160° respectively. Cu2 is surrounded by three nitrogen atoms, one oxygen atom and one thiocyanate. The thiocyanate coordinates linearly to Cu2. The e_3 dihedral angle between the N2−N5−N39 and N2−N5−N49 planes is 15.9°. Therefore Cu2 is assigned to have a distorted SP coordination geometry. It is interesting to note that the Cu2−O1 distance of 2.23(1) Å is the shortest of all Cu−O distances in Table 3 which is 0.06 Å shorter than those in **1** and **4**. This bond distance is also shorter than the Cu-O distances in Cu_2(HL-H)$Cl_n(ClO)_{4-n}$ complexes (2.32−2.72 Å) reported previously.[14] Since only three anions were detected by the X-ray diffraction method; therefore, besides the structure formulated for **5**, the possibility that the hydroxy group in HL-H is deprotonated while the OH^- counterion is a water, cannot be ruled out. However, the Cu-O distances in the deprotonated complexes $[Cu_2(\mu\text{-}X)(L\text{-}Et^-)]^{2+}$ (X= N_3^-, OAc^-, NO_2^-)[3−5] are in the range 1.85−2.157 Å which is shorter than that in **5**. Furthermore, the endogenous RO^-, if it exists, is not in the expected bridging mode as in $[Cu_2(\mu\text{-}X)(L\text{-}Et^-)]^{2+}$ (X = N_3^-, OAc^-, NO_2^-).[3−5] Hence, it is judged that a formula of $Cu_2(L\text{-}H^-)(NCS)_3$·3$H_2O$·3$CH_3OH$·$Et_2O$ for **5** is unlikely.

Discussion

The structures of five dicopper complexes with the HL-H ligand were determined. The anions are thiocyanate(s) in combination with chloride(s) (in **1** and **4**) or perchlorate anions (**2** and **3**). In **5**, only three thiocyanate anions were detected without any other counter anion. From the long Cu-O distance as well as the coordination mode of the oxygen atom, it was judged that the proton of the endogenous hydroxy group is not dissociated and an uncoordinated hydroxy group is present to maintain charge balance. The different bonding environments of copper ions in these five complexes are depicted.



1



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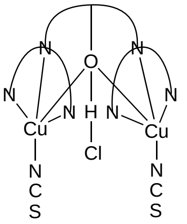

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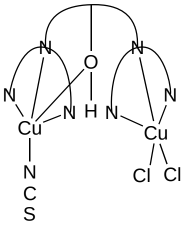
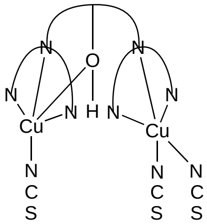


4



5

3 and **5** were prepared from Cu(II) salts which were obtained by oxidizing Cu(I) aerobically. Some ions in them (H_3O^+ in **3** and OH^- in **5**) are not found in the complexes prepared directly from Cu(II) salt. **5** is likely a minor product, the major product is Cu_2(HL-H)$(NCS)_3(ClO_4)$·4H_2O which also has three thiocyanate anions. The coordination environments of the copper ions in this major product should be the same as those in **5**.

The e_3 dihedral angles for Cu(II) ions coordinated by at least one chloride ion (Cu1 in **1** and Cu1 in **4**) are noticeably smaller than the other e_3 angles.

Each copper ion is invariably coordinated by the three tripodal nitrogen atoms consisting of an amino nitrogen N_{am} and two imino nitrogen atoms N_{ar} of the benzimidazolyl groups. The other coordinating ligands such as thiocyanate and chloride are free to move to locations for maximum stability or minimum energy for each copper center. Hence, the $N_{am}N_{ar2}$ coordination arrangement must provide the driving force for each copper ion to be in the prevailing pentacoordinated structure. The bond angles in Table 4 reveal that N_{ar}−Cu−N_{ar} angles are mostly within a narrow range of 155−159°. However, there are three angles slightly smaller in the range 146−151°. These small angles correlate with the greater dihedral angles e_3 with the exception of Cu1 in **5** which possesses both large e_3 and N_{ar}−Cu−N_{ar} angles. All N_{ar}−Cu−N_{am} angles are also in a narrow range of 79−85°. The sum of the two N_{am}−Cu−N_{ar} angles is always slightly larger than ∠N_{ar}−Cu−N_{ar}. It indicates that the copper ion is out of the plane of the tripodal nitrogen atoms. Furthermore, the Cu ions are also located beyond the Na_{ar}−N_{ar}

lines away from N_{am}. All these geometrical considerations indicate that the tripodal nitrogen coordination site cannot possibly form a square copper complex, which is a common Cu(II) coordination geometry. Therefore, when Cu ion is coordinated by the three nitrogen atoms in one of the coordination site of HL-H, it is forced to assume five coordination. The geometrical features of the tripodal nitrogen coordination site are similar to those reported for $Cu_2(HL\text{-}H)Cl_n^{4-n}$ ($n = 2$ and 4).[14] In the hemocyanin model complexes of $HBPz_3$ developed by Kitajima et. al,[8-13] tripodal N_3 coordination site also forces the Cu(II) ions in the oxy state to assume pentacoordination. In the absence of another coordinating ligand, the only way for Cu ions to have pentacoordination is that O_2 must be coordinated by the μ_2:η^2:η^2 mode in $O_2Cu_2(HBPz_3)_2$. The copper coordination environment in hemocyanin formed by the three imino nitrogen atoms of histidine residues must be similar to that in HL-H and $HBPz_3$ in the sense that the tripodal N_3 coordination site can force a pentacoordination for Cu(II). Since the Cu−Cu distances in deoxy-Hc and oxy-Hc are approximately equal, it is likely that the tripodal nitrogen coordination sites remain essentially the same whether O_2 binds or not.

Since most of the N_{am}−Cu distances are within the range 2.06−2.13 Å, the Cu1−N1 distances of 2.17, 2.20, and 2.21 Å for **1**, **4**, and **5**, respectively, seem somewhat large. These large distances correlate with the exceptional small N1−Cu1−N4 (N1−Cu1−Cl1 for **4**) angles (141−158°) which are normally in the range 174−178° for the remaining copper coordination environments including those of Cu2. Furthermore, they also correlate with the distances of Cu1 above the square pyramidal planes. In these Cu1 coordination environments, the sums of ∠N1−Cu1−N19 and ∠N1−Cu1−N29 are much closer to ∠N19−Cu1−N29 (160, 161, and 160° vs 157, 156, and 157° for **1**, **4**, and **5**, respectively) than the other Cu coordination environments where the difference between these values are about 10°. It indicates that Cu1 is very close to the plane of N1−N19−N29. To maximize the bonding to N19 and N29 in the plane, Cu1 was drawn away from N1 resulting in a large Cu1−N1 distance.

The Cu(II)−Cu(II) distances are in the range 4.45−7.99 Å. The magnetic interaction between the two copper ions in each complex is expected to be small. Consistent with this expectation, the magnetic susceptibility data of **2** ($J = -0.384(7)$ cm^{-1}) and **4** ($J = -0.36(1)$ cm^{-1}) indicate that the magnetic exchange interaction between the copper ions is negligibly small. The bridging hydroxy group may provide an effective pathway for the magnetic interaction between the two copper ions in **2** and **3**. However, the magnetic susceptibility data of **2** as well as the fact that the EPR spectra of complexes **1**−**5** can be detected show that this pathway is not effective.

The isotropic g values (2.15) estimated from the broad EPR spectra of **1**−**5** are slightly larger than those (1.99 for **2** and 2.00 for **4**) determined from the magnetic susceptibility data by fitting to a model consisting of pairs of intramolecularly interacting Cu(II) ions. These discrepancies are likely due to the presence of intermolecular interaction among Cu(II) ions which was neglected in the analysis of magnetic susceptibility data. A similar discrepancy between g values determined from the EPR spectrum and magnetic susceptibility data has also appeared in the literature.[15] The principal values of **g** and **A** tensors are expected to be very different for Cu(II) ions in SQ and TBP coordination environments.[30] Though we were able to determine the structures of **1**−**5** where the Cu(II) ions are in highly distorted SQ and TBP environments, the broadness of the EPR spectra prevented us from making an in-depth analysis.

From the results of our previous report[14] and this work, HL-H proves to be very flexible in its coordination to form dinuclear copper complex. Depending on the nature of the accompanying anion(s), several different bonding modes of this ligand were observed in the X-ray determined structures. They can be divided into the following four categories. In type I, the structure is represented by $N_3CuX_a(\mu\text{-OHR})\ CuN_3X_b$. The ligands X_a, X_b, and others used in the following discussion may be the same or different. It is characterized by the presence of an endogenous protonated hydroxy group bridging between the two copper ions. The type II structure can be represented by $N_3CuX_a(OHR)CuN_3X_bX_c$ which is characterized by a protonated nonbridging alcoholic hydroxy group. The type III structure represented by $N_3Cu(\mu\text{-X})(\mu\text{-OR})CuN_3$, is characterized by the presence of a bridging external ligand and an endogenous bridging alkoxide group. The type IV structure represented by $[N_3CuX_a(OHR)CuN_3(\mu\text{-X}_b)]_2$, is characterized by the presence of a hydroxy group and exogenous ions bridge between two dicopper complexes. **2** and **3**, the second and third reported structures next to $Cu_2(HL\text{-}H)Cl_2(ClO_4)_2$,[14] are examples of the first type of structure. **1**, **4**, and **5** as well as $[Cu_2(HL\text{-}H)Cl_3]Cl$[14] are examples of the second type of structure. Complexes of type III with X of N_3^-, NO_2^-, or OAc$^-$ are known.[3-5] The copper ions in these complexes are constrained to be close to each other, and the nearly planar N_3Cu arrangement leads to a trigonal bipyramidal coordination environment for Cu with X and RO$^-$ in the axial positions. $[Cu_2(HL\text{-}H)Cl(\mu\text{-Cl})]_2$[14] is a unique example of the type IV structure.

It is possible to deduce the order of coordinating ability of ligands coordinated to the N_3Cu fragment of the dicopper complexes of HL-H by examining the compositions of the structurally characterized complexes. When there are four coordinating anions in a complex, the endogenous hydroxy group always coordinates terminally (denoted as OHR(t)), and one anion is not coordinating. There is no tetrathiocyanate complex being isolated in spite of the presence of sufficient amount of NCS$^-$ in the preparation of **5**. In the complex with three thiocyanate ions the proton of the hydroxy group is not dissociated. It is an indication that NCS$^-$ is unable to replace OHR(t). In the NCS$^-$ and Cl$^-$ mixed complexes, only Cl$^-$ is forced out of the coordination sphere. Thus, NCS$^-$ has a better coordinating ability than Cl$^-$. When only two chloride anions are present, structures with either bridging chloride (Cl$^-$(b)) or bridging hydroxy (OHR(b)) are observed.[14] Therefore, these bridging ligands must have comparable stability. The relative coordinating ability can thus be summarized in the following sequence: OHR(t) > NCS$^-$ > Cl$^-$(t) > OHR(b) ≈ Cl$^-$(b).

In the preparation of $Cu_2(HL\text{-}H)Cl_n(ClO_4)_{4-n}$ ($n = 2$ and 4)[14] addition of base failed to deprotonate the hydroxy group. It indicates that the tendency of the endogenous coordinated hydroxy group to become an terminally coordinated OR$^-$(t) or bridging OR$^-$(b) is rather small. The presence of azide ligand also failed to deprotonate OHR(t) to become OR$^-$(t) or OR$^-$(b) in the presence of chloride ions. Though bidentate bridging ligand, such as azide, is capable of forming complexes with OR$^-$(b), OR$^-$(b) can exist only under the condition that no other ligand with reasonable coordinating ability is present.

In complexes **1**−**5**, the copper ions which are already coordinated by OHR(b) or OHR(t), are also coordinated by NCS$^-$ ion. The theory that hard ligand prefers to coordinate to hard metal ion and soft ligand prefers to coordinate to soft metal ion can be used to rationalize this structural feature. OHR(t) is a hard ligand which renders the copper ion hard.

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(30) Porte, L. A. In *Electron Spin Resonance*; A specialist Periodical Report, The Royal Society of Chemistry; London, 1980; Vol. 6, Chapter 5.

Therefore, Cu2 in **1** and **4** are favorably coordinated by NCS^- rather than by the soft Cl^-. Since each Cu(II) favors pentacoordination, hence the second NCS^- ligand in **1** therefore coordinates to Cu1. Therefore the two NCS^- ions coordinate to two different copper ions. In **4**, Cu1 is coordinated by two chloride ions. This can be explained by the fact that the Cu1 which is soft due to coordination by a soft Cl^- ion is favorably coordinated by another soft chloride ion. In **3**, the effect of the hardness of OHR(b) goes to the extreme of leaving one chloride not coordinated.

With the above sequence of coordinating ability together with the tendency of Cu(II) ion to form a five-coordinated complex after being coordinated by the tripodal nitrogen atoms, it is possible to predict the structures of dicopper complexes of HL-H. For example, if the complex has only one monodentate coordinating anion, then at least one solvent must coordinate to Cu and the hydroxy group assumes the ROH(b) coordination mode if the solvent is not strongly coordinating. In the case where the ligating anion can bridge the two copper ions favorably, such as N_3^-, NO_2^- and OAc^-, then deprotonation of hydroxy group to become RO^-(b) is favored. If there are two monodentate coordinating ligands, then a structure with OHR(b) is most likely. However, if one of the ligand has the tendency to be a bridging ligand, such as Cl^- then the structure of type IV is also possible. If there are three monodentate coordinating ligands, then the structure with OHR(t) and two of the harder ligands (including OHR(t)) are coordinated to the same copper ion. If there are four coordinating ligands, then a structure the same as that with three coordinating ligands is predicted provided the coordinating abilities of these ligands are not all stronger than OHR(t). Only electronic effects are considered in the above prediction; steric effects could also have large effect on the structure.

Since the $\mu_2:\eta^2:\eta^2$-coordinated dioxygen dicopper complexes of $HBPz_3$ can reproduce the spectroscopic characteristics of oxyhemocyanin, there is no doubt that this coordination mode of dioxygen is the most likely one in oxyhemocyanin. A model compound with a ligand which contains a tripodal nitrogen coordination environment with the constraint that Cu(II) ion cannot form a planar complex is a necessary condition to be a good choice. However, the model compound containing an endogenous hydroxy group OHR as in HL-H cannot be a good system. The OHR which has been demonstrated to have a high coordinating ability, can coordinate to a Cu(II) ion. Thus dioxygen is prevented to be in a $\mu_2:\eta^2:\eta^2$ coordination mode. Likewise, a model compound with a phenoxide group is also not a good choice since phenoxide is a strong coordinating ligand.

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Supporting Information Available: Figures showing experimental data and nonlinear least-squares analysis of the magnetic susceptibilities of **2** and **4** and tables of crystal data and intensity collection conditions, atomic coordinates, thermal parameters, bond distances, bond angles, and least-square planes for complexes **1**−**5** (59 pages). Ordering information is given on any current masthead page.

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