

Self-Assembly, Structures, and Magnetic Properties of Ladder-Like Copper(II) Coordination Polymers

Kil Sik Min and Myunghyun Paik Suh¹

School of Chemistry and Center for Molecular Catalysis, Seoul National University, Seoul 151-742, Republic of Korea

Two novel ladder-like copper(II) compounds, $[\text{Cu}_2(\text{histamine})_2(\text{C}_2\text{O}_4)(\text{ClO}_4)_2]$ (1) and $[\text{Cu}_2(\text{histamine})_2(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_2(\text{NO}_3)_2]$ (2), are prepared. Compound 1 crystallizes in the triclinic space group $P\bar{1}$, with $a = 7.450(4)$ Å, $b = 7.519(7)$ Å, $c = 9.646(5)$ Å, $\alpha = 85.78(7)^\circ$, $\beta = 88.60(4)^\circ$, $\gamma = 76.78(7)^\circ$, $V = 524.5(6)$ Å³, and $Z = 1$ with $R = 0.0789$ (all data). In 1, the dinuclear units of $[\text{Cu}_2(\text{histamine})_2(\text{C}_2\text{O}_4)]^{2+}$ are linked together by the perchlorate anions to form a ladder-like chain. The chains interact each other by the π - π stacking interactions via the imidazole groups. Compound 2 crystallizes in the triclinic space group $P\bar{1}$, with $a = 7.579(2)$ Å, $b = 8.133(1)$ Å, $c = 9.161(3)$ Å, $\alpha = 77.06(2)^\circ$, $\beta = 89.23(2)^\circ$, $\gamma = 82.54(1)^\circ$, $V = 545.6(2)$ Å³, and $Z = 1$ with $R = 0.0751$ (all data). In 2, each dinuclear unit $[\text{Cu}_2(\text{histamine})_2(\text{C}_2\text{O}_4)]^{2+}$ is coordinated with a nitrate anion and a water molecule, and they are held together by the hydrogen bonding interactions to form a ladder-like chain. The magnetic susceptibility data of 1 and 2 measured in 2–300 K provide the magnetic parameters, $g = 2.08$, $J = -166$ cm⁻¹, $J' = 6.46$ cm⁻¹, $\rho = 0.0026$, $N\alpha = 155 \times 10^{-6}$ cm³ mol⁻¹, and $R = 1.03 \times 10^{-3}$ ($g = 2.05$, $J = -162$ cm⁻¹, $J' = 10.5$ cm⁻¹, $\rho = 0.0029$, and $R = 2.95 \times 10^{-3}$ with the fixed value of $N\alpha = 120 \times 10^{-6}$ cm³ mol⁻¹) for 1 and $g = 2.00$, $J = -158$ cm⁻¹, $J' = 26.5$ cm⁻¹, $\rho = 0.0020$, $N\alpha = 136 \times 10^{-6}$ cm³ mol⁻¹, and $R = 7.31 \times 10^{-4}$ ($g = 2.01$, $J = -157$ cm⁻¹, $J' = 25.0$ cm⁻¹, $\rho = 0.0021$, and $R = 1.32 \times 10^{-3}$ with the fixed value of $N\alpha = 120 \times 10^{-6}$ cm³ mol⁻¹) for 2. These indicate that very strong antiferromagnetic interactions occur along the rungs of the ladder via the oxalate bridge and weak ferromagnetic interactions along the chains.

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Key Words: ladder-like compounds; copper(II) complexes; stacking interactions; hydrogen bond; antiferromagnetism; coordination polymer; structure.

INTRODUCTION

The crystal engineering of one- (1D), two- (2D), and three-dimensional (3D) coordination polymers is of great

¹To whom correspondence should be addressed. Fax: 82-2-886-8516. E-mail: mpsuh@snu.ac.kr.

interest (1–6) because of the novel topologies of the compounds and their physicochemical properties such as magnetism and electrical conductivity. We have been interested in ladder-like coordination polymers containing paramagnetic metal centers to see how the magnetic exchange-coupling interactions occur between the adjacent metal ions. The oxalate-bridged dicopper(II) complexes (7) would be the good candidates for building the ladder-like compounds since the two copper(II) ions in the dimeric unit can coordinate other bridging ligands at the axial positions. Dicopper(II) complexes containing oxalato bridging ligands have been studied as potential models for binuclear copper metalloprotein active sites (8, 9). They were also employed for the investigation of exchange-coupling interactions between adjacent metal ions (10, 11). The oxalato ligand is known to mediate the magnetic interactions between the two metal centers connected by the ligand (11, 12).

In this paper, we report the structures and magnetic properties of two ladder-like copper(II) coordination polymers, $[\text{Cu}_2(\text{histamine})_2(\text{C}_2\text{O}_4)(\text{ClO}_4)_2]$ (1) and $[\text{Cu}_2(\text{histamine})_2(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_2(\text{NO}_3)_2]$ (2), which are self-assembled by CuX_2 ($X = \text{ClO}_4^-$ and NO_3^-), histamine, and oxalate in water.

EXPERIMENTAL

General Methods

All chemicals and solvents used in the synthesis were of reagent grade and used without further purification. Infrared spectra were recorded with a Perkin Elmer 2000 FT-IR spectrophotometer. Elemental analyses were performed by the analytical laboratory of Seoul National University. UV/vis diffuse reflectance spectra were recorded with a Cary 300 Bio UV/vis spectrophotometer. Magnetic susceptibility was measured in the temperature range of 2–300 K at 1 T on a Quantum Design MPMS superconducting quantum interference device (SQUID). Diamagnetic corrections were made by using Pascal's constants.



Synthesis Safety Note

Although we have experienced no problem with the compounds reported in this work, perchlorate salts of metal complexes with organic ligands are often explosive and should be handled with great caution.

$[Cu_2(histamine)_2(C_2O_4)(ClO_4)_2]$, **1**

To the aqueous solution (50 mL) of $Cu(ClO_4)_2 \cdot 5H_2O$ (3.92 g, 10.6 mmol), were slowly added an aqueous solution (20 mL) containing histamine dihydrochloride (1.95 g, 10.6 mmol) and sodium hydroxide (0.85 g, 21 mmol), and the aqueous solution (50 mL) of sodium oxalate (0.71 g, 5.3 mmol). The mixture was stirred for 1 h at room temperature. The solution was allowed to stand in a refrigerator until blue-violet crystals formed, which were filtered off, washed with water, and dried in air. Yield: 83%. Anal. Calcd for $Cu_2C_{12}H_{18}N_6Cl_2O_{12}$: C, 22.65; H, 2.85; N, 13.21. Found: C, 22.61; H, 2.62; N, 13.52. FT-IR (Nujol mull, cm^{-1}): 3315(s), 3264(s), 3162(s), 1651(s), 1586(s), 1506(m), 1358(s), 1313(m), 1275(m), 1221(m), 1090(s), 933(m), 799(m), 622(s), 488(m). UV/vis (diffuse reflectance spectrum, λ_{max}): 649 nm.

$[Cu_2(histamine)_2(C_2O_4)(H_2O)_2(NO_3)_2]$, **2**

To the aqueous solution (30 mL) of $Cu(NO_3)_2 \cdot 3H_2O$ (1.97 g, 8.15 mmol) were slowly added the aqueous solution (20 mL) containing histamine dihydrochloride (1.50 g, 8.15 mmol) and sodium hydroxide (0.65 g, 16 mmol) and then the aqueous solution (40 mL) of sodium oxalate (0.55 g, 4.1 mmol). The mixture was stirred for 1 h at room temperature. The solution was allowed to stand in a refrigerator until blue-violet crystals formed, which were filtered off, washed with water, and dried in air. Yield: 75%. Anal. Calcd for $Cu_2C_{12}H_{22}N_8O_{12}$: C, 24.12; H, 3.71; N, 18.76. Found: C, 24.07; H, 3.26; N, 18.84. FT-IR (Nujol mull, cm^{-1}): 3294(s), 3259(s), 3157(s), 1651(s), 1580(s), 1507(m), 1376(s, br), 1271(s), 1140(s), 1061(m), 938(m), 800(s), 624(m), 483(m). UV/vis (diffuse reflectance spectrum, λ_{max}): 655 nm.

X-Ray Diffraction Measurements

Single crystals of **1** ($0.3 \times 0.5 \times 0.7$ mm) and **2** ($0.5 \times 0.5 \times 0.7$ mm) were mounted on an Enraf-Nonius CAD4 diffractometer. The unit cell parameters were determined from 25 machine-centered reflections with $22 \leq 2\theta \leq 29^\circ$ for **1** and $22 \leq 2\theta \leq 28^\circ$ for **2**. Intensities were collected with graphite-monochromated $MoK\alpha$ radiation, using the ω - 2θ scan. Three standard reflections were measured every 2 h as orientation and intensity control and no significant intensity decay was observed. Lorentz and polarization corrections were made. No absorption correction was made. The

TABLE 1
Crystallographic Data for $[Cu_2(histamine)_2(C_2O_4)(ClO_4)_2]$ (**1**)
and $[Cu_2(histamine)_2(C_2O_4)(H_2O)_2(NO_3)_2]$ (**2**)

	1	2
Formula	$Cu_2C_{12}H_{18}N_6Cl_2O_{12}$	$Cu_2C_{12}H_{22}N_8O_{12}$
fw	636.30	597.45
Crystal system	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a (Å)	7.450(4)	7.579(2)
b (Å)	7.519(7)	8.133(1)
c (Å)	9.646(5)	9.161(3)
α (°)	85.78(7)	77.06(2)
β (°)	88.60(4)	89.23(2)
γ (°)	76.78(7)	82.54(1)
V (Å ³)	524.5(6)	545.6(2)
Z	1	1
d_{calc} (g cm ⁻³)	2.014	1.818
λ (Å)	0.71069	0.71069
T (K)	293(2)	293(2)
Max θ (°)	25	25
μ (mm ⁻¹)	2.359	2.027
Unique data	1331	1894
Observed data [$I > 2\sigma(I)$]	1229	1553
Parameter refined	154	154
GO F	1.101	1.096
$F(000)$	320	304
R_1^a (all data)	0.0789	0.0751
wR_2^b (all data)	0.2015	0.1852

Note. $w = 1/[\sigma^2(F_o^2) + (0.1698P)^2 + 0.5444P]$, where $P = (F_o^2 + 2F_c^2)/3$ for **1**. $w = 1/[\sigma^2(F_o^2) + (0.1177P)^2 + 0.8899P]$, where $P = (F_o^2 + 2F_c^2)/3$ for **2**.

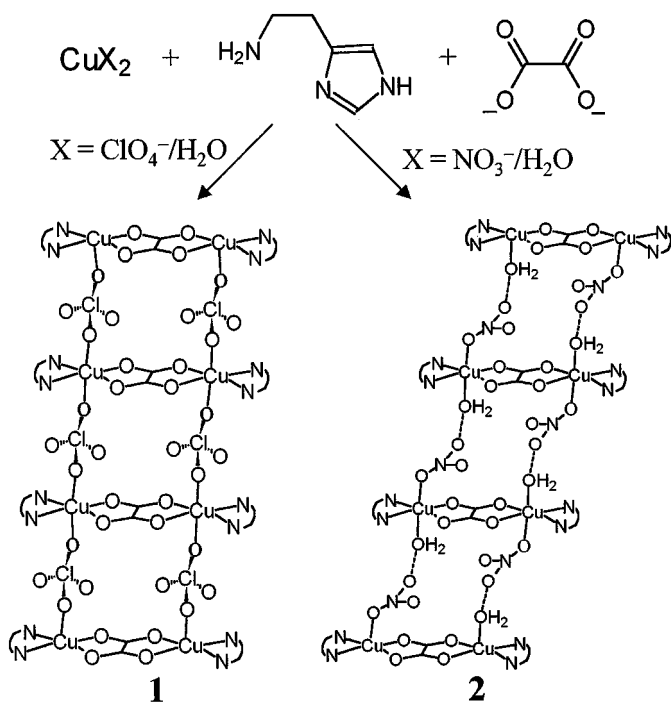
$$^a R_1 = \sum \|F_o\| - |F_c| / \sum \|F_o\|$$

$$^b wR_2(F^2) = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$$

crystal structures for **1** and **2** were solved by Patterson methods (13) and refined by full-matrix least-squares methods using the program SHELXL97 (14). The positions of all nonhydrogen atoms were refined with anisotropic displacement factors. Calculated positions of all hydrogen atoms were allowed to ride on their bonded atoms with the isotropic displacement factors fixed with values of 1.2 times those of the bonded atoms. The crystallographic data of **1** and **2** are summarized in Table 1.

RESULTS AND DISCUSSION

Compounds **1** and **2** were prepared by the self-assembly of CuX_2 ($X = ClO_4^-$ and NO_3^-) with histamine and sodium oxalate in H_2O (Scheme 1). They were characterized by the elemental analysis, IR spectra, UV/vis diffuse reflectance spectra, and single crystal X-ray diffraction analysis. Compound **1** is soluble in water and in organic solvents such as DMF and DMSO, but insoluble in MeCN and MeNO₂. Compound **2** is soluble in water and in organic solvents such as DMF, MeOH, and DMSO, but insoluble in MeCN and MeNO₂. The infrared spectra (Nujol mull) of **1** and **2**



SCHEME 1

show $\nu(\text{CN})$ of imidazole groups at 1506 and 1507 cm^{-1} , respectively, $\nu(\text{ClO}_4^-)$ at 1090 cm^{-1} , and $\nu(\text{NO}_3^-)$ at 1300 cm^{-1} . In **1**, N-H stretching frequencies of primary amines appear at 3264 and 3315 cm^{-1} while those of **2** appear at 3157 and 3259 cm^{-1} , respectively. The $\nu(\text{CO}_2^-)$ of oxalate in **1** and **2** occurs at 1651 cm^{-1} . UV/vis diffuse reflectance spectra indicate that d-d transitions of **1** and **2** occur at 649 and 655 nm , respectively. The values of molar conductance (Λ_M) are $213\text{ }\Omega^{-1}\text{ cm}^{-1}\text{ M}^{-1}$ for **1** and $255\text{ }\Omega^{-1}\text{ cm}^{-1}\text{ M}^{-1}$ for **2** in H_2O , which correspond to the 1:2 electrolytes (15, 16). This indicates that the ladder-like chains are dissociated to the dinuclear units when they are dissolved in H_2O .

Crystal Structures

$[\text{Cu}_2(\text{histamine})_2(\text{C}_2\text{O}_4)(\text{ClO}_4)_2]$, **1**. An ORTEP drawing of **1** is shown in Fig. 1a and selected bond distances and angles are listed in Table 2. The coordination geometry around copper(II) ion is a tetragonally distorted octahedron. The copper(II) ion is coordinated by two nitrogens of a histamine, two oxygens of an oxalate, and two oxygens of two perchlorate anions. The average $\text{Cu}-\text{N}_{\text{histamine}}$ and $\text{Cu}-\text{O}_{\text{oxalate}}$ bond distances are $1.958(4)$ and $1.992(3)\text{ \AA}$, respectively. The bite distances of the five-membered and six-membered chelate rings are $2.660(6)$ and $2.876(7)\text{ \AA}$, respectively. The bite angles of five-membered and six-membered chelate rings are $83.9(2)^\circ$ and $94.7(2)^\circ$, respectively. Perchlorate anions link dimeric units by coordinating cop-

per(II) ions apically, which leads to a ladder-like chain extending along the a axis (Fig. 1b). The octahedron is elongated along the $\text{O}4'-\text{Cu}-\text{O}3''$ axis ($' = -x, -y + 1, -z + 1$ and $'' = -x + 1, -y + 1, -z + 1$) due to the Jahn-Teller distortion of copper(II) ion. The apical $\text{Cu}-\text{O}3''$ and $\text{Cu}-\text{O}4'$ bond distances are $2.699(8)$ and $2.709(8)\text{ \AA}$, respectively. The copper(II) ion is $0.036(3)\text{ \AA}$ out of the square-coordination plane toward $\text{O}3''$ atom. The two copper(II) ions within the dinuclear unit are connected by a bis-bidentate oxalato ligand with an inversion center located at the center of the carbon-carbon bond of the oxalato anion. The shortest $\text{Cu}\cdots\text{Cu}$ contact within the dimer is $5.167(5)\text{ \AA}$ and the shortest $\text{Cu}\cdots\text{Cu}$ distance along the chain is $7.450(4)\text{ \AA}$, although they are separated by four bonds. Between the ladder chains, coordinated imidazole groups undergo the offset $\pi-\pi$ stacking interactions, which propagate along the c axis (Fig. 1c) (17). The dihedral angle between two imidazole planes is $\theta = 0.0^\circ$, and the shortest interatomic distance between the imidazole groups is $3.325(16)\text{ \AA}$ [$\text{C}5\cdots\text{C}5(-x, -y + 1, -z)$]. The interplanar separation between the imidazoles is $2.97\text{--}3.00\text{ \AA}$. Due to this offset $\pi-\pi$ stacking interactions, the structure becomes two-dimensional. In addition, the imidazole groups of the

TABLE 2
Selected Bond Distances (\AA) and Angles ($^\circ$) for
 $[\text{Cu}_2(\text{histamine})_2(\text{C}_2\text{O}_4)(\text{ClO}_4)_2]$ (**1**)^a

Cu-N1	1.972(5)	N3-C5	1.328(8)
Cu-N3	1.938(6)	N3-C3	1.372(8)
Cu-O1	1.984(5)	C1-C2	1.519(11)
Cu-O2	1.997(4)	C2-C3	1.489(9)
Cu-O3''	2.699(8)	C3-C4	1.337(10)
Cu-O4'	2.709(8)	C6-C6'	1.553(10)
O1-C6	1.226(8)	Cl1-O3	1.430(7)
O2-C6'	1.246(8)	Cl1-O4	1.386(7)
N1-C1	1.447(9)	Cl1-O5	1.411(6)
N2-C5	1.336(9)	Cl1-O6	1.424(6)
N2-C4	1.354(10)		
N3-Cu-N1	94.7(2)	C4-C3-N3	107.9(6)
N3-Cu-O1	93.2(2)	C4-C3-C2	130.7(7)
N1-Cu-O1	172.0(2)	N3-C3-C2	121.4(6)
N3-Cu-O2	173.6(2)	C3-C4-N2	107.9(6)
N1-Cu-O2	88.3(2)	N3-C5-N2	109.4(6)
O1-Cu-O2	83.9(2)	O1-C6-O2'	126.7(5)
C6-O1-Cu	111.0(3)	O1-C6-C6'	118.1(7)
C6'-O2-Cu	111.5(3)	O2'-C6-C6'	115.1(7)
C1-N1-Cu	119.0(4)	O4-C11-O5	109.1(5)
C5-N2-C4	107.7(6)	O4-C11-O6	108.9(5)
C5-N3-C3	107.1(6)	O5-C11-O6	108.4(5)
C5-N3-Cu	126.5(5)	O4-C11-O3	109.3(5)
C3-N3-Cu	126.4(4)	O5-C11-O3	110.2(5)
N1-C1-C2	111.1(7)	O6-C11-O3	110.9(5)
C4-C3-N3	107.9(6)		

^a Symmetry transformations used to generate equivalent atoms: prime, $-x, -y + 1, -z + 1$; double prime, $-x + 1, -y + 1, -z + 1$.

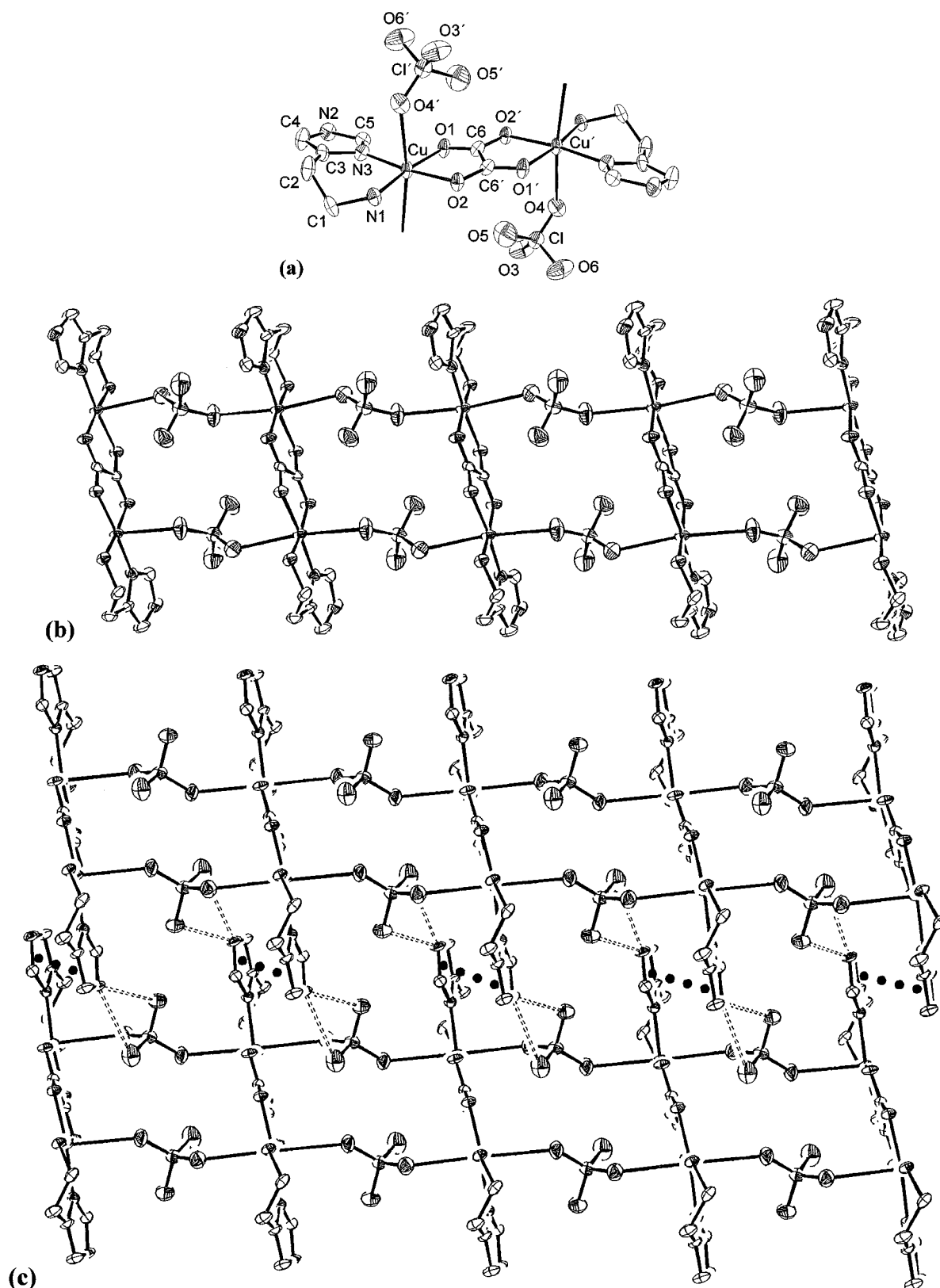


FIG. 1. (a) ORTEP drawing of 1 with atomic numbering scheme ($' = -x, -y + 1, -z + 1$). The atoms are represented by 40% probable thermal ellipsoids. (b) Perspective view of 1, showing a ladder-like 1D chain. (c) Extended 2D structure of 1. The hydrogen bonding interactions are indicated as ---. The π - π stacking interactions between the ladder-like chains via imidazole groups are indicated as •••.

histamine moieties are involved in weak hydrogen bonding interactions with the oxygen atoms of the perchlorate anion coordinating copper(II) ions of the adjacent ladder chains: $N2 \cdots O5(x, y, z-1)$, 3.219(11) Å; $N2-H2 \cdots O5(x, y, z-1)$,

172.6°; $N2 \cdots O6(x, y, z-1)$, 3.124(10) Å; $N2-H2 \cdots O6(x, y, z-1)$, 124.3°.

$[Cu_2(histamine)_2(C_2O_4)(H_2O)_2(NO_3)_2]$, **2**. An ORTEP drawing of the compound **2** is shown in Fig. 2a and selected

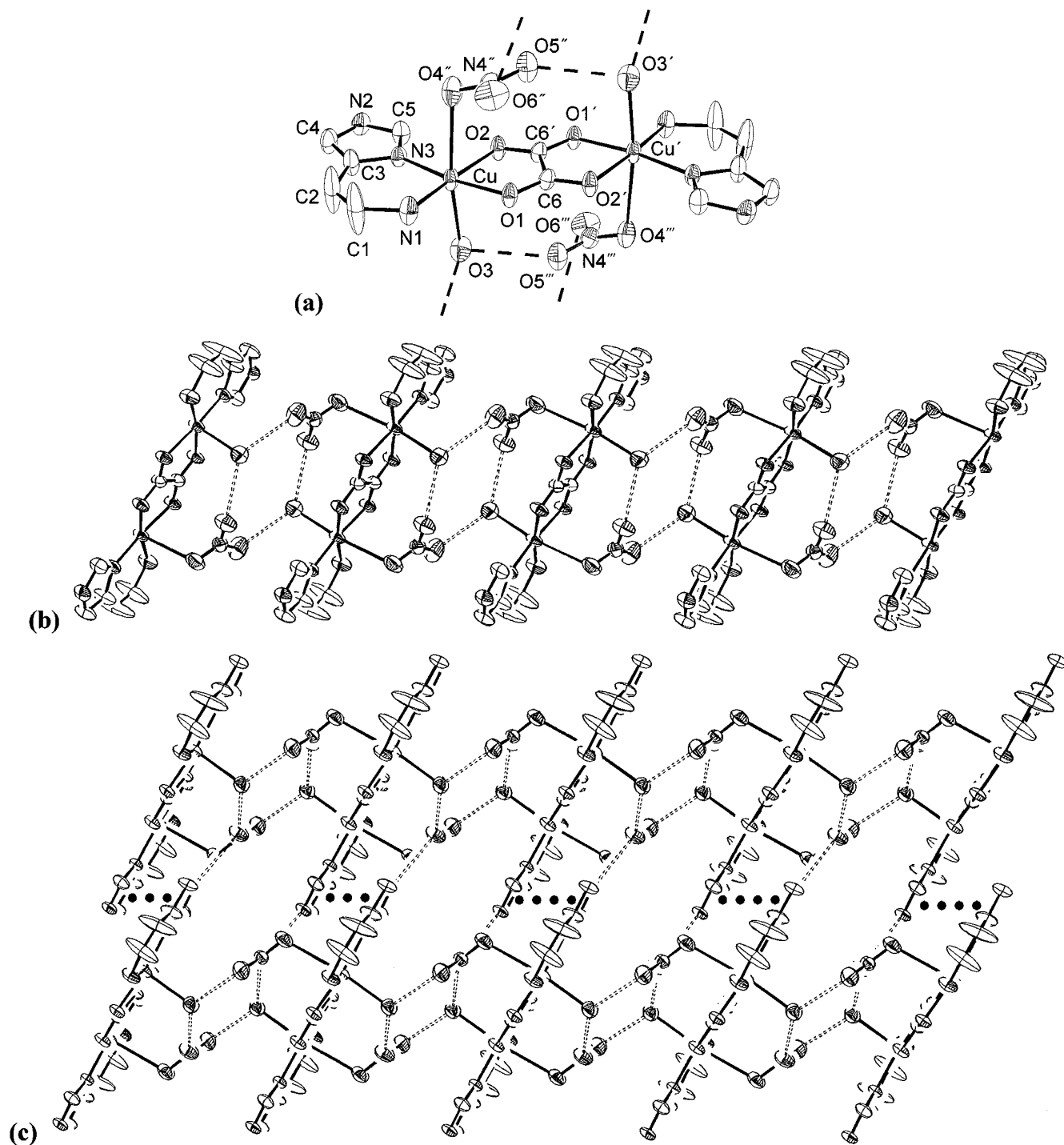


FIG. 2. (a) ORTEP drawing of **2** with atomic numbering scheme ($' = -x + 1, -y, -z$, $'' = x, y - 1, z$, and $''' = -x + 1, -y + 1, -z$). The atoms are represented by 30% probable thermal ellipsoids. (b) Perspective view of **2** showing the ladder-like 1D chains. (c) Extended 2D structure of **2**. The hydrogen bonding interactions are indicated as ---. The π - π stacking interactions between the ladder-like chains via imidazole groups are indicated as •••.

TABLE 3
Selected Bond Distances (Å) and Angles (°) for
[Cu₂(histamine)₂(C₂O₄)(H₂O)₂(NO₃)₂] (2)^a

Cu–N1	1.976(5)	N3–C3	1.370(8)
Cu–N3	1.949(4)	C1–C2	1.198(12)
Cu–O1	2.003(4)	C2–C3	1.486(11)
Cu–O2	2.004(4)	C3–C4	1.327(10)
Cu–O3	2.319(6)	C6–O2'	1.239(7)
Cu–O4''	2.735(6)	C6–O1	1.242(7)
N1–C1	1.433(10)	C6–C6'	1.555(11)
N2–C5	1.302(8)	N4–O4	1.240(8)
N2–C4	1.330(9)	N4–O5	1.240(8)
N3–C5	1.316(8)	N4–O6	1.228(8)
N3–Cu–N1	95.1(2)	C2–C1–N1	131.4(8)
N3–Cu–O1	173.0(2)	C1–C2–C3	127.5(8)
N1–Cu–O1	88.3(2)	C4–C3–N3	107.9(6)
N3–Cu–O2	92.8(2)	C4–C3–C2	131.2(7)
N1–Cu–O2	170.9(2)	N3–C3–C2	120.8(6)
O1–Cu–O2	83.3(2)	C3–C4–N2	107.7(6)
N3–Cu–O3	96.3(2)	N2–C5–N3	110.8(6)
N1–Cu–O3	92.8(3)	O2'–C6–O1	126.9(5)
O1–Cu–O3	89.6(2)	O2'–C6–C6'	116.4(6)
O2–Cu–O3	90.9(2)	O1–C6–C6'	116.6(6)
C1–N1–Cu	119.1(5)	C6–O1–Cu	111.7(3)
C5–N2–C4	108.0(5)	C6'–O2–Cu	111.9(4)
C5–N3–C3	105.5(5)	O6–N4–O4	120.7(7)
C5–N3–Cu	128.5(4)	O6–N4–O5	121.0(6)
C3–N3–Cu	126.0(4)	O4–N4–O5	118.3(6)

^aSymmetry transformations used to generate equivalent atoms: prime, $-x + 1, -y, -z$; double prime, $x, y - 1, z$.

bond distances and angles are listed in Table 3. The copper(II) dimeric unit is the same as that in **1** and the coordination geometry around copper(II) ion in the dimer is also a distorted octahedron. The apical sites of a copper(II) ion are coordinated with a water molecule and a nitrate anion. The octahedral coordination geometry around copper(II) ion is elongated along the O3–Cu–O4'' axis ($'' = x, y - 1, z$). The copper(II) ion is 0.089(3) Å out of the square-coordination plane toward O3 atom. The average Cu–N_{histamine} and Cu–O_{oxalate} bond distances are 1.960(3) and 2.004(3) Å, respectively. The bite distances of the five-membered and six-membered chelate rings are 2.664(5) and 2.895(7) Å, respectively. The bite angles of five-membered and six-membered chelate rings are 83.3(2)° and 95.1(2)°, respectively. The apical Cu–O3 and Cu–O4'' bond distances are 2.319(6) and 2.735(6) Å, respectively, indicating that nitrate ion weakly coordinates copper(II) ion. Within the dinuclear unit, the water molecule coordinating a copper(II) ion forms a hydrogen bond with the nitrate anion binding the other copper(II) ion: O3···O5''' ($''' = -x + 1, -y + 1, -z$), 2.887(8) Å. The dinuclear units are held together by the hydrogen bonding interactions between the nitrate ion coordinating a unit and the water molecule coordinating the

adjacent unit (O3···O6, 2.827(9) Å) to form a ladder-like chain, which propagates along the *b* axis (Fig. 2b). In addition, the imidazole groups of the histamine moieties are involved in hydrogen bonding interactions with the oxygen atoms of the nitrate anions coordinating copper(II) ions of the adjacent chains: N2···O5($-x + 1, -y + 1, -z + 1$), 2.977(7) Å; N2–H2···O5($-x + 1, -y + 1, -z + 1$), 167.0°. The shortest Cu···Cu distance within the dimeric unit is 5.212(2) Å. The shortest Cu···Cu distance along the chain is 8.133(1) Å. Similar to **1**, between the ladder-like chains, imidazole groups undergo offset π - π stacking interactions with the dihedral angle of $\theta = 0.0^\circ$. The shortest interatomic distance and the interplanar separation between the imidazole groups are 3.488(12) Å [C5···C5($-x + 1, -y, -z + 1$)] and 3.11–3.12 Å, respectively. Due to the offset π - π stacking interactions (17), the compound becomes a 2-D sheet extending along the (200) plane (Fig. 2c).

Magnetic Properties

The magnetic behaviors of compounds **1** and **2** are illustrated in Figs. 3 and 4. For both compounds, the value of χ_M decreases as the temperature is lowered up to 50 K, which indicates a very strong antiferromagnetic interaction, and then increases as the temperature is lowered to 2 K, which is indicative of paramagnetic impurities. For the ladder-like chains, the spin exchange might occur along the rungs (the intradimeric interaction) and along the chains (the interdimeric one). For the compounds **1** and **2**, however,

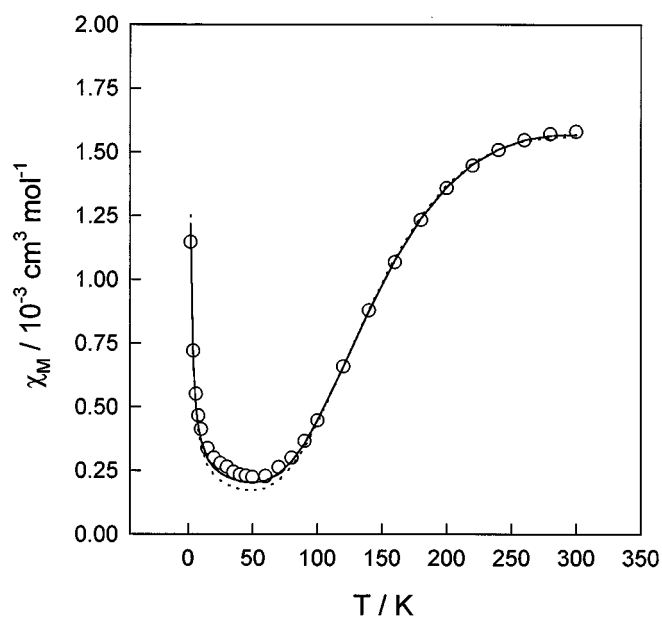


FIG. 3. Plot of χ_M vs T for **1**. The solid line represents the best-fit curve to Eq. [2]. The dotted line is the best-fit curve when the value of Nz is fixed as $120 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$.

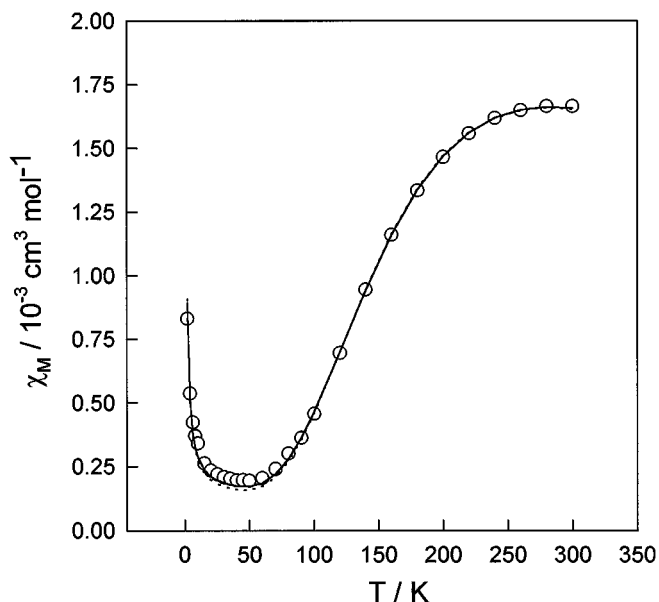


FIG. 4. Plot of χ_M vs T for **2**. The solid line represents the best-fit curve to Eq. [2]. The dotted line is the best-fit curve when the value of $N\alpha$ is fixed as $120 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$.

the extended pathways involve bridging perchlorate anion and hydrogen bonding interactions between water molecule and nitrate anion, respectively, and thus spin exchange along the chains may be weak. Therefore, compounds **1** and **2** were regarded as an assembly of “quasi” isolated dimers, and the expression (Eq. [1]) derived from the spin Hamiltonian $H = -2J\sum S_1 \cdot S_2 + g\beta H(S_1 + S_2)$ was employed for a pair of exchange-coupled $S = 1/2$ ions, with consideration of the external field (7, 11, 18):

$$\chi_M = \frac{2N\beta^2 g^2}{3kT} [1 + \frac{1}{3} \exp(-2J/kT)]^{-1}. \quad [1]$$

Residual *interdimeric* interactions through the perchlorate and nitrate anions were accounted for by the addition of mean field term to Eq. [1] (11, 19). The equation for the susceptibility will then have the form of Eq. [2], where J' is the interdimeric coupling constant and z is the number of interacting neighbors. In Eq. [2], contribution of the paramagnetic impurity and temperature-independent paramagnetism were also taken into account:

$$\chi'_M = \chi_M / [1 - (2zJ'/N\beta^2 g^2)\chi_M] (1 - \rho) + \left(\frac{N\beta^2 g^2}{2kT} \right) \rho + N\alpha. \quad [2]$$

The best fit parameters for the magnetic susceptibility data to Eq. [2] are $g = 2.08$, $J = -166 \text{ cm}^{-1}$, $J' =$

6.46 cm^{-1} , $\rho = 0.0026$, $N\alpha = 155 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$, and $R = 1.03 \times 10^{-3}$ ($g = 2.05$, $J = -162 \text{ cm}^{-1}$, $J' = 10.5 \text{ cm}^{-1}$, $\rho = 0.0029$, and $R = 2.95 \times 10^{-3}$ with the fixed value of $N\alpha = 120 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$) (20) for **1**, and $g = 2.00$, $J = -158 \text{ cm}^{-1}$, $J' = 26.5 \text{ cm}^{-1}$, $\rho = 0.0020$, $N\alpha = 136 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$, and $R = 7.31 \times 10^{-4}$ ($g = 2.01$, $J = -157 \text{ cm}^{-1}$, $J' = 25.0 \text{ cm}^{-1}$, $\rho = 0.0021$, and $R = 1.32 \times 10^{-3}$ with the fixed value of $N\alpha = 120 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$) (20) for **2** (R is defined as $\sum [(\chi_M)_{\text{calc}} - (\chi_M)_{\text{obsd}}]^2 / \sum [(\chi_M)_{\text{obsd}}]^2$). The J values of **1** and **2** indicate that oxalate anion mediates a strong antiferromagnetic coupling between two copper(II) ions separated by ca. 5 Å. The data are compared with other oxalato-bridged dicopper(II) compounds in Table 4. For the present ladder-like supramolecular compounds, very strong antiferromagnetic interactions occur along the rungs of the ladder via the oxalato bridge and weak ferromagnetic interactions occur along the ladder chains where the $\text{Cu} \cdots \text{Cu}$ separation is rather long (7.5–8.1 Å).

CONCLUSIONS

Two ladder-like copper(II) coordination polymers $[\text{Cu}_2(\text{histamine})_2(\text{C}_2\text{O}_4)(\text{ClO}_4)_2]$ (**1**) and $[\text{Cu}_2(\text{histamine})_2(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_2(\text{NO}_3)_2]$ (**2**), in which copper(II) dinuclear units are held together by ClO_4^- and NO_3^- , respectively, have been prepared. Compounds **1** and **2** give rise to 2D structures due to the hydrogen bonding and π - π stacking interactions between the ladder-like chains via imidazole groups of histamine ligands. The coordination polymers show very strong antiferromagnetism along the rungs of the ladder via the oxalate bridge and weak ferromagnetism along the ladder chains.

TABLE 4
Magnetic Parameters for Copper(II) Oxalate Dimers

Compound ^a	J (cm^{-1})	g	ρ	Ref.
$[\text{Cu}_2(\text{histamine})_2(\text{C}_2\text{O}_4)(\text{ClO}_4)_2]$ (1)	-166	2.08	0.0026	This work
$[\text{Cu}_2(\text{histamine})_2(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_2(\text{NO}_3)_2]$ (2)	-158	2.00	0.0020	This work
$[\text{Cu}_2(\text{tmen})_2(\text{C}_2\text{O}_4)(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot 1.25\text{H}_2\text{O}$	-193	2.16	0.051	21
$[\text{Cu}_2(\text{mepirizole})_2(\text{C}_2\text{O}_4)(\text{ClO}_4)_2]$	-175	2.20	0	22
$[\text{Cu}_2(\text{mepirizole})_2(\text{C}_2\text{O}_4)(\text{NO}_3)_2]$	-156	2.12	0.0004	22
$[\text{Cu}_2(\text{HBIP})_2(\text{C}_2\text{O}_4)(\text{Cl})_2] \cdot 2\text{H}_2\text{O}$	-133	2.13	0.01	7
$[\text{Cu}_2(\text{BIP})_2(\text{C}_2\text{O}_4)] \cdot 2\text{H}_2\text{O}$	-54	2.15	0.02	7
$[\text{Cu}_2(\text{Et}_5\text{dien})_2(\text{C}_2\text{O}_4)](\text{BPh}_4)_2$	-37	2.26	0.02	23

^atmen, *N,N,N',N'*-tetramethylethylenediamine; mepirizole, 4-methoxy-2-(5-methoxy-3-methyl-pyrazol-1-yl)-6-methylpyrimidine; HBIP, 3,3-bis(2-imidazolyl)propionic acid; BIP, 3,3-bis(2-imidazolyl)propionate; Et₅dien, 1,1,4,7,7-pentamethyldiethylenetriamine.

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