μ -Phenolato- μ -acetato-bridged Dinuclear Copper(II) Complex with Dinucleating Schiff-base Ligand Having Three Phenolate Groups

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The μ -phenolato- μ -acetato-bridged dinuclear copper(II) complex with 2-(5-chloro-2-hydroxyphenyl)-1,3-bis(2-(5-chloro-2-hydroxybenzylideneamino)ethyl)imidazolidine (H_3L), $[Cu_2(L)(\mu-CH_3CO_2)]$, was synthesized. The crystal structure was determined by the single-crystal X-ray diffraction method at 293 K. The complex crystallized as $[Cu_2(L)(\mu-CH_3CO_2)] \cdot CH_3CN \cdot H_2O$ in the monoclinic space group $P2_1/c$ with $a = 9.088(6)$, $b = 13.296(9)$, $c = 29.20(2) \text{ \AA}$, $\beta = 95.131(13)^\circ$, $V = 3514(4) \text{ \AA}^3$, $D_{\text{calcd}} = 1.520 \text{ g/cm}^3$, $Z = 4$. The $R1$ [$I > 2\sigma(I)$] and $wR2$ (all data) values are 0.0512 and 0.1282, respectively, for all 8308 independent reflections. The two copper(II) atoms are bridged by phenolato-oxygen of L^{3-} and μ -acetato, where each copper(II) atom is further coordinated by phenolato-oxygen, imino- and imidazolidine-nitrogen atoms of L^{3-} in a meridional fashion to form a square-pyramidal geometry. The temperature dependence of the magnetic susceptibilities showed a ferromagnetic interaction with $J = +4.3 \text{ cm}^{-1}$ between the two copper(II) atoms.

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Schiff-base ligand, 2-(5-chloro-2-hydroxyphenyl)-1,3-bis(2-(5-chloro-2-hydroxybenzylideneamino)ethyl)imidazolidine (H_3L) is an interesting dinucleating ligand, because it has three phenolate groups within the imidazolidine ligand and gives unique dinuclear lanthanide complexes.¹ So far, some dinuclear metal complexes with related Schiff-base ligands have been reported.²⁻⁵ We have engaged in synthetic studies on dinuclear copper(II) complexes with Schiff-base ligands.⁶⁻⁸ In this study, we isolated a dinuclear copper(II) complex with L^{3-} , and determined the crystal structure of this complex, which has not yet been reported, as shown in Fig. 1. This paper describes the crystal structure of $[Cu_2(L)(\mu-CH_3CO_2)] \cdot CH_3CN \cdot H_2O$. The synthetic method and the magnetic property are also described.

H_3L was synthesized by the following procedure with some modification of the literature method.^{2,3} A solution of 0.213 g (1.46 mmol) of triethylenetetramine in 8 cm³ of ethanol was added to a solution of 0.700 g (4.47 mmol) of 5-chlorosalicylaldehyde in 8 cm³ of ethanol. The reaction

mixture was stirred and heated for 1 h to give a yellow precipitate. The precipitate was isolated by filtration and washed with ethanol and dried at room temperature, yielding 0.774 g (94.4%). *Anal.* Found: C, 57.83; H, 5.06; N, 10.29%. Calcd for $C_{27}H_{27}Cl_3N_4O_3$: C, 57.71; H, 4.84; N, 9.97%. IR (KBr, cm⁻¹): $\nu(C=N)$ 1633.

$[Cu_2(L)(\mu-CH_3CO_2)]$. To an acetonitrile solution (10 cm³) of H_3L (54.0 mg, 0.0961 mmol) was added an acetonitrile solution (5 cm³) of copper(II) acetate (35.8 mg, 0.197 mmol); the mixed solution was then stirred for 1 h. The resulting solution was filtered and the filtrate was left standing at room temperature for several days to give green crystals. The crystals were collected. Yield, 52.8 mg (68.8% based on H_3L). *Anal.* Found: C, 43.32; H, 3.81; N, 6.92%. Calcd for $C_{29}H_{33}Cl_3Cu_2N_4O_8$ $[Cu_2(L)(\mu-CH_3CO_2)] \cdot 3H_2O$: C, 43.59; H, 4.16; N, 7.01%. IR (KBr, cm⁻¹): $\nu(C=N)$ 1645, $\nu_{as}(COO^-)$ 1574, $\nu_s(COO^-)$ 1461. Diffused reflectance spectra, λ_{max} : 242, 386, 718, 1000 nm. Absorption spectra (in methanol), λ_{max} : 384 nm ($\epsilon = 9260 \text{ M}^{-1} \text{ cm}^{-1}$, CT band (phenolate(O) $\rightarrow$ Cu)),^{6,7} 652 nm ($\epsilon = 400 \text{ M}^{-1} \text{ cm}^{-1}$, d-d band).⁷

A preliminary examination was made, and data were collected on a Bruker CCD X-ray diffractometer (SMART APEX) using graphite-monochromated Mo- $K\alpha$ radiation. Crystal data and details concerning the data collection are given in Table 1. The structure was solved by an intrinsic phasing method and refined by full-matrix least-squares methods. The hydrogen atoms, except for the water molecule, were inserted at their calculated positions, and fixed there. All of the calculations were carried out on a Windows 7 Core i7 computer utilizing SHELXT-2014/4 and SHELXL-2014/7.⁹ Crystallographic data have been deposited with Cambridge Crystallographic Data Centre (Deposit numbers CCDC-1849887). Copies of the data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Fax, +44 1223 336033; e-mail, deposit@ccdc.cam.ac.uk).

Fig. 1 Chemical structure of the title compound.

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Table 1 Crystal and experimental data

Chemical formula: $C_{31}H_{32}Cl_3Cu_2N_5O_6$
Formula weight = 804.04
$T = 293$ K
Crystal system: monoclinic
Space group: $P2_1/c$
$a = 9.088(6)$ Å
$b = 13.296(9)$ Å
$c = 29.20(2)$ Å
$V = 3514(4)$ Å ³
$Z = 4$
$D_x = 1.520$ g/cm ³
Radiation: Mo $K\alpha$ ($\lambda = 0.71073$ Å)
$\mu(\text{Mo } K\alpha) = 1.487$ mm ⁻¹
$F(0\ 0\ 0) = 1640$
Crystal size = $0.12 \times 0.13 \times 0.32$ mm ³
No. of reflections collected = 22212
No. of independent reflections = 8308
θ range for data collection: 1.40 to 28.76°
Data/Restraints/Parameters = 8308/0/434
Goodness-of-fit on $F^2 = 0.977$
R indices [$I > 2\sigma(I)$]: $R1 = 0.0512$, $wR2 = 0.1044$
R indices (all data): $R1 = 0.1110$, $wR2 = 0.1282$
$(\Delta/\sigma)_{\max} = 0.002$
$(\Delta\rho)_{\max} = 0.423$ eÅ ⁻³
$(\Delta\rho)_{\min} = -0.493$ eÅ ⁻³
Measurement: Bruker Smart APEX CCD diffractometer
Program system: SHELXTL
Structure determination: intrinsic phasing (SHELXT-2014/4)
Refinement: full matrix least-squares (SHELXL-2014/7)
CCDC deposition number: 1849887

Fig. 2 ORTEP drawing of $[Cu_2(L)(\mu\text{-CH}_3\text{CO}_2)]$, showing the thermal ellipsoids at the 50% probability level. Hydrogen atoms are omitted for clarity.

The asymmetric unit consists of one dinuclear molecule $[Cu_2(L)(\mu\text{-CH}_3\text{CO}_2)]$, one acetonitrile, and one water molecule. The dinuclear molecule was drawn by the ORTEP program in Fig. 2. In the dinuclear molecule, the two copper(II) atoms are bridged by a phenolato-oxygen of L^{3-} and μ -acetato, where each copper(II) atom is further coordinated by phenolato-oxygen, imino- and imidazolidine-nitrogen atoms of L^{3-} in a meridional fashion to form a five-coordinate geometry. The τ values¹⁰ of the Cu1 and Cu2 atoms are 0.177 and 0.233, respectively, showing distorted square-pyramidal geometries. It is to be noted that the acetate ion bridges the two copper atoms in a *syn-syn* mode,¹¹ giving a comparatively long Cu1–Cu2 distance of 3.328(2) Å (Table 2). In the crystal, water molecule (O6) are hydrogen-bonded to the phenolato-oxygen atoms (O1, O2, and

Table 2 Selected bond distances (Å) and angles ($^\circ$)

Cu1–Cu2	3.328(2)	Cu2–O2	1.993(3)
Cu1–O1	1.930(3)	Cu2–O3	1.944(3)
Cu1–O2	1.980(3)	Cu2–O5	2.150(3)
Cu1–O4	2.179(3)	Cu2–N3	2.116(3)
Cu1–N1	1.955(3)	Cu2–N4	1.955(3)
Cu1–N2	2.140(3)		
Cu1–O2–Cu2	113.81 (13)		

Table 3 Hydrogen-bonding geometry (Å, $^\circ$)

D–H...A	D–H (Å)	H...A (Å)	D...A (Å)	D–H...A ($^\circ$)
O6–H6A...O1	0.666	2.299	2.926	157.95
O6–H6B...O2	0.711	2.635	2.971	111.58
O6–H6B...O3	0.711	2.202	2.905	170.74

Fig. 3 Packing diagram of the title compound. Hydrogen atoms are omitted for clarity. Dashed lines show hydrogen bonds between the phenolato-oxygen atoms of the dinuclear complex and water molecule.

O3) of L^{3-} , as shown in Table 3 (Fig. 3). The coordination geometries around the copper atoms and the molecular structure found in this study are similar to those of the dinuclear copper(II) complex with the bromo-derivative of the related Schiff-base ligands, although the crystal structure is different from the present one.⁵

The diffused reflectance spectrum of the complex showed a CT band at 386 nm and a broad d-d band 718 nm with shoulder around 1000 nm. The d-d band feature is in agreement with the square-pyramidal geometry around the copper(II) ions.¹² The absorption spectrum confirmed the assignment of the spectra, although the shoulder around 1000 nm could not be detected. A magnetic susceptibility measurement was performed with a Quantum Design SQUID susceptometer in the temperature range of 4.5 – 300 K. The magnetic moment per copper(II) atom is $2.01 \mu_B$ at 300 K. This value is larger than the spin-only value of copper(II) ($1.73 \mu_B$, $S = 1/2$). As shown in Fig. 4, the moment takes an almost constant value until 60 K with lowering of the temperature, and then increases, reaching a maximum value of $2.16 \mu_B$ at 4.5 K. The magnetic data were analyzed by the Bleaney–Bowers equation (1) based on a consideration for

Fig. 4 Temperature dependence of the magnetic susceptibilities (red circle), magnetic moment (blue square), and the fitting curves with the parameters in the text of the title compound.

the exchange interaction ($2J$) and temperature independent paramagnetism (tip) of the copper(II) ions:¹³

$$\chi_A = (Ng^2\beta^2/3kT)[1 + 1/3\exp(-2J/kT)]^{-1} + tip \quad (1)$$

The best fitting afforded the parameters $J = +4.3 \text{ cm}^{-1}$, $g = 2.25$, and $tip = 60 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$. The magnetic property is also similar to that of the dinuclear copper(II) complex with the bromo-derivative of the related Schiff-base ligands.⁵

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