

Dicopper(II) and Dicadmium(II) Complexes of Double-Tweezer Ligand with Thiopyridine Moiety

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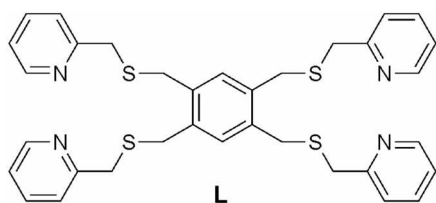
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Interest in binuclear complexes has long been generated by the prospect that such species may serve as models of electron transfer, charge transfer and allosteric behaviors observed in biochemical system.¹⁻³ In particular, dicopper complexes coordinated by histidine N-donor and S-containing thiolate or sulfide ligands comprise the active sites of key metalloproteins.^{4,5} Accordingly, an approach to the structure and functions of the copper centers is to develop model dicopper-multidentate ligand systems incorporating N and S donors.⁶ Recently, Hanton *et al.*⁷ introduced a flexible ligand with four thiopyridyl arms **L** [1,2,4,5-tetrakis(2-pyridylmethylsulfanyl)methyl)benzene] which forms a dinuclear complex with Cd(NO₃)₂ instead of a polymeric array due to the unusual three-layered π -stacking motif. Since **L** is expected as a double-tweezer type dinucleating ligand toward a range of metal ions, we have carried out the self-assembly of **L** with copper(II) and cadmium(II) perchlorates. In this paper, we report two binuclear complexes [Cu₂L(ClO₄)₂(DMF)₂](ClO₄)₂·2DMF (**1**) and [Cd₂L(ClO₄)₂·(CH₃OH)₂](ClO₄)₂ (**2**), which were structurally characterized by single-crystal X-ray analysis.



Results and Discussion

Preparation and Crystal Structure of L Complex with Copper(II) Perchlorate (1). The ligand **L** was synthesized according to the procedure previously reported.⁷ An emerald green complex precipitate was obtained from the reaction of Cu(ClO₄)₂·6H₂O in methanol with **L** in dichloromethane. Single crystals of **1** suitable for X-ray analysis were obtained by vapor diffusion of diethyl ether into DMF solution of this complex. The X-ray analysis revealed that **1** is a discrete-type dicopper(II) complex of formula [Cu₂L(ClO₄)₂(DMF)₂](ClO₄)₂·2DMF (Figure 1). A summary of bond lengths and angles in the coordination sphere of each copper(II) in **1** is given in Table 1. Since there

is an imposed inversion at the center of central aromatic group, asymmetric unit of the complex part of **1** contains a half molecule of **L**, one Cu atom, one ClO₄⁻ ion and one DMF. Each Cu atom is effectively six-coordinated. The octahedral Cu atom is coordinated by two pyridyl N atoms (N1 and N2) and one S atom (S2) of the ligand and one carbonyl O atom (O1) of one DMF in the equatorial positions. One S (S1) atom of the ligand and one O atom from one monodentate OClO₃⁻ occupy the axial position [\angle O2-Cu1-S1 170.9(1)^o]. The mean plane defined by the atoms in the equatorial base is planar within 0.28 Å. As expected, the apical monodentate perchlorate and S2 atom show elongated bond lengths [Cu1-S1 2.576(1), Cu1-O2 2.660(3) Å] when compared with those for the equatorial ones [Cu1-S2 2.329(1), Cu1-O1 1.993(3) Å]. The bond lengths of Cu1-N(pyridine) [Cu1-N1 1.999(4), Cu1-N2 2.009(4) Å] in the equatorial positions (trans) lie at the

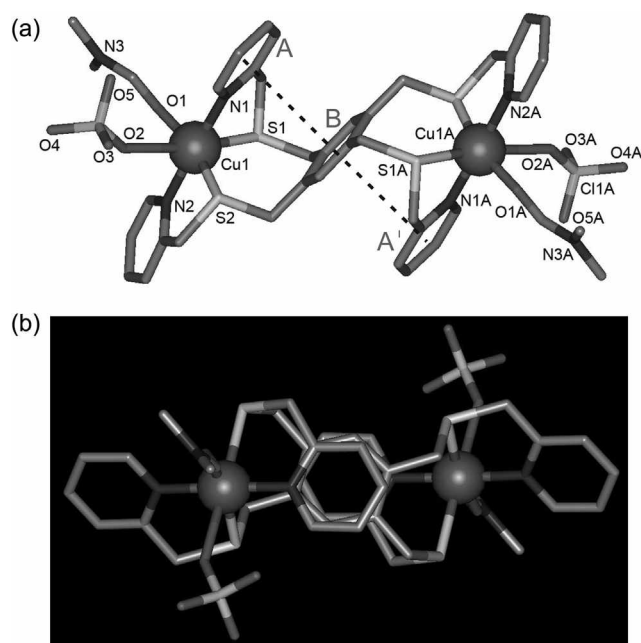


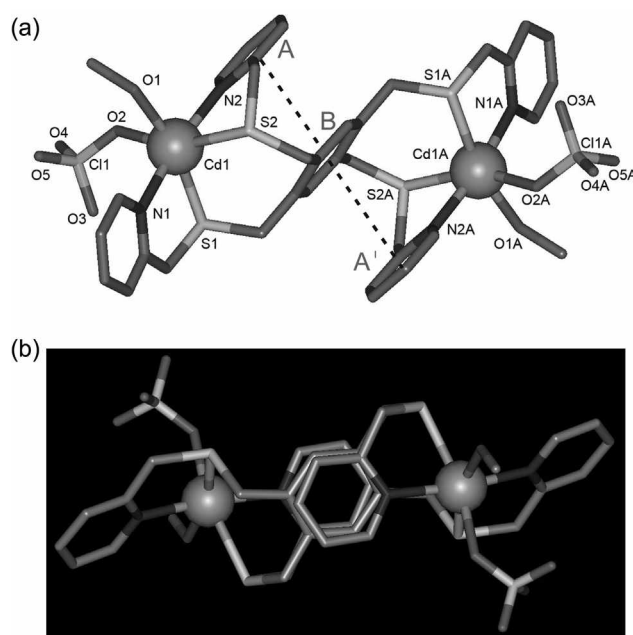
Figure 1. (a) Crystal structure of **1**, [Cu₂L(ClO₄)₂(DMF)₂](ClO₄)₂·2DMF showing π - π stacking interactions (dashed lines) and (b) top view. Hydrogen atoms, noncoordinating anions and solvent molecules are omitted. Symmetry operation: (A) $-x+1, -y+1, -z+1$.

Table 1. Selected bond lengths [Å] and bond angles [°] for **1**, [Cu₂L(ClO₄)₂(DMF)₂](ClO₄)₂·2DMF

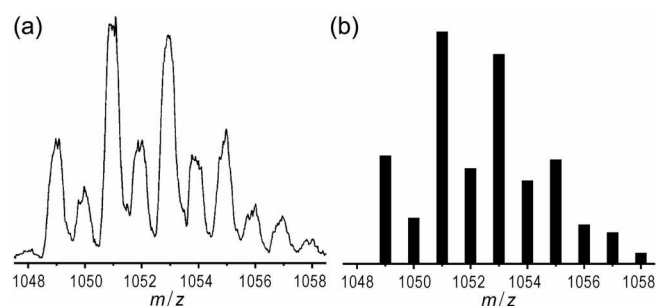
Cu1-O1	1.993(3)	Cu1-O2	2.660(3)
Cu1-N1	1.999(4)	Cu1-N2	2.009(4)
Cu1-S1	2.576(1)	Cu1-S2	2.329(1)
O1-Cu1-N1	93.0(1)	O1-Cu1-N2	89.8(1)
O1-Cu1-S1	86.6(1)	O1-Cu1-S2	163.2(1)
O2-Cu1-S1	170.9(1)	O2-Cu1-S2	79.1(1)
O2-Cu1-N1	94.9(1)	O2-Cu1-N2	85.2(1)
O1-Cu1-O2	84.5(1)	N1-Cu1-N2	177.2(2)
N1-Cu1-S1	83.3(1)	N1-Cu1-S2	92.1(1)
N2-Cu1-S1	97.0(1)	N2-Cu1-S2	85.2(1)
S1-Cu1-S2	109.9(1)		

middle of the reported range (1.967–2.058 Å).^{8–11} The Cu···Cu separation in **1** is 9.021(1) Å. Two perchlorate ions and two DMF molecules exist in the crystal lattice without significant interaction (not shown). Additionally, the intraligand π - π stacking is another major interaction in this structure (see dashed lines in Figure 1a). As illustrated in Figure 1b, two terminal pyridine (rings A and A') and central aromatic unit (ring B) are arranged so that they form face-to-face type π - π stacking interaction (dihedral angle 23.2°, centroid-to-centroid distance 3.75 Å). This motif has been observed in other related systems with flexible thioether-pyridine arms.^{12–14} Such folding obviously rigidify the dinucleating complex structure and also may induce the open space which leads the participation of the solvent and anion coordination because of the unsaturation of coordination sphere of metal center.

Preparation and Crystal Structure of L Complex with Cadmium(II) Perchlorate (2). Having successfully obtained dicopper(II) complex **L**, we proceeded to the preparation of **L** complex with cadmium(II) system. In case of cadmium(II) perchlorate complex **2**, a colorless crystalline product suitable for X-ray analysis was obtained from methanol solution of **L** layered with methanol solution of Cd(ClO₄)₂·4H₂O. The X-ray analysis revealed that **2** is also a dinuclear complex of formula [Cd₂L(ClO₄)₂(CH₃OH)₂](ClO₄)₂ (Figure 2). A summary of bond lengths and angles in the coordination sphere of each cadmium(II) in **2** is given in Table 2. The cadmium(II) center is also in a hexa-coordinated environment and the coordination is best described as octahedral with some noticeable distortions. Hanton *et al.*⁷ reported similar dicadmium(II) nitrate complex of **L** which has, however, seven and eight coordinate Cd(II) centers. The coordination sites of Cd(II) centers in **2** are occupied by N₂S₂ donors of **L**, one monodentate ClO₄⁻ ion and one methanol molecule. The Cd···Cd separation in **1** is 8.952(2) Å. Two perchlorate ions exist in the crystal lattice without significant interaction (not shown). The arrangement of central aromatic ring (B) and two terminal pyridine rings (A and A') are quite parallel to each other, displaying face-to-face π - π stacking interactions (dashed lines in Figure 2a; dihedral angle 17.0°, centroid-to-centroid distance 3.57 Å).

**Figure 2.** (a) Crystal structure of **2**, [Cd₂L(ClO₄)₂(CH₃OH)₂](ClO₄)₂ showing π - π stacking interactions (dashed lines) and (b) top view. Hydrogen atoms and non-coordinating anions are omitted. Symmetry operation: (A) $-x+3/2, -y+1/2, -z+1$.**Table 2.** Selected bond lengths [Å] and bond angles [°] for **2**, [Cd₂L(ClO₄)₂(CH₃OH)₂](ClO₄)₂

Cd1-O1	2.300(1)	Cd1-O2	2.402(7)
Cd1-N1	2.315(9)	Cd1-N2	2.309(9)
Cd1-S1	2.631(3)	Cd1-S2	2.747(3)
O1-Cd1-N2	91.4(4)	O1-Cd1-N1	90.7(4)
O1-Cd1-S1	166.1(2)	O1-Cd1-S2	84.2(2)
O2-Cd1-S1	88.3(2)	O2-Cd1-S2	159.4(2)
O2-Cd1-N1	103.1(3)	O2-Cd1-N2	85.4(3)
O1-Cd1-O2	86.8(3)	N1-Cd1-N2	171.3(3)
N1-Cd1-S1	77.7(3)	N1-Cd1-S2	95.5(2)
N2-Cd1-S1	101.2(3)	N2-Cd1-S2	76.4(2)
S1-Cd1-S2	104.4(1)		

**Figure 3.** (a) Observed isotopic distribution for [Cu₂L(ClO₄)₂]⁺ in the FAB mass spectrum of **1** and (b) predicted mass spectral distribution for this ion.

Based on the bond angles around the metal center, **2** [76.4(2)–104.4(1)°] is slightly less distorted from octahedral

Table 3. Crystal data and structure refinement

	1	2
Chemical formula	C ₄₆ H ₅₂ Cl ₄ Cu ₂ N ₈ O ₂₀ S ₄	C ₃₆ H ₄₂ Cd ₂ Cl ₄ N ₄ O ₁₈ S ₄
Crystal system	Triclinic	Monoclinic
Space group	P-1	C2/c
a (Å)	8.7370(7)	22.587(2)
b (Å)	12.2117(9)	10.9726(11)
c (Å)	15.3811(12)	20.538(2)
α (°)	85.754(2)	90
β (°)	83.582(2)	105.735(2)
γ (°)	75.611(2)	90
V	1577.8(2)	4899.2(8)
Z	1	4
F(000)	744	2632
D _c (g/cm ³)	1.520	1.781
M (mm ⁻¹)	1.050	1.331
R	0.0494	0.0768
wR	0.1231	0.2019

geometry than 1 [79.1(1)-109.9(1)^o].

The FAB mass spectrum of the complex **1** was obtained (Figure 3). The mass spectrum of **1** contains peak at *m/z* 1051, which corresponds to [Cd₂L(ClO₄)₃]⁻. The relative abundance of its isotope pattern is in good agreement with that of simulated one.

In summary, a double-tweezer type ligand **L** with four thiopyridine moieties was employed in the assembly reactions with some metal perchlorates and its dicopper(II) (**1**) and dicadmium(II) (**2**) complexes in crystalline state were isolated. In octahedral environments of **1** and **2** coordinated by N₂S₂ donors, one anion and one solvent molecule, ligand **L** adopted a folded conformation, displaying an intraligand three-layer π-π stacking arrangement between the central ring and two pyridine rings in both ends.

Experimental Section

Generals. All commercial reagents including solvents were of analytical reagent grade. Mass spectra were obtained on a JEOL JMS-700 spectrometer (FAB) at the Central Laboratory of Gyeongsang National University. Infrared spectra were measured with a Mattson Genesis Series FT-IR spectrophotometer. Melting points are uncorrected.

[Cu₂L(ClO₄)₂(DMF)₂](ClO₄)₂·2DMF (**1**). Reaction of Cu(ClO₄)₂·6H₂O (65.0 mg, 0.17 mmol) in methanol with **L** (50.0 mg, 0.08 mmol) in dichloromethane afforded emerald green precipitate. Vapor diffusion of diethyl ether into DMF solution of the precipitate afforded green-colored crystalline product. Mp 160-162 °C (decomp.). IR (KBr, cm⁻¹): 2950, 1604, 1485, 1440, 1396, 1108 (s, ClO₄⁻), 773.

[Cd₂L(ClO₄)₂(CH₃OH)₂](ClO₄)₂ (**2**). Colorless crystalline product was obtained from methanol solution of **L**

(50.0 mg, 0.08 mmol) layered with methanol solution of Cd(ClO₄)₂·4H₂O (67.3 mg, 0.17 mmol). Mp 195-196 °C (decomp.). IR (KBr, cm⁻¹): 2921, 1596, 1473, 1436, 1108 (s, ClO₄⁻), 752.

Crystallography. All data were collected on a Bruker SMART diffractometer equipped with a graphite monochromated MoKa (λ = 0.71073 Å) radiation source and a CCD detector; 45 frames of two-dimensional diffraction images were collected and processed to obtain the cell parameters and orientation matrix. The two-dimensional diffraction images were collected, each of which was measured at -100 °C. The structure was solved by a direct method and refined by full matrix least square against *F*² for all data. All non-H atoms were refined with anisotropic displacement parameters. All hydrogen atoms were included in calculated position with isotropic thermal parameters 1.2 times those of attached atoms.

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Supplementary material. Supplementary crystallographic data associated to complexes **1** and **2** have been deposited at the Cambridge Crystallographic Data Centre, CCDC No 683507 and 683508. Copies of the data can be obtained free of charge on application to CCDC, 12 Union road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk) or electronically *via* www.ccdc.cam.ac.uk/data_request/cif.

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