

Doubly Supported Cyclodimer. Structural Features of Copper(II) Nitrate with 1,4-Bis(dimethyl-3-pyridylsilyl)benzene

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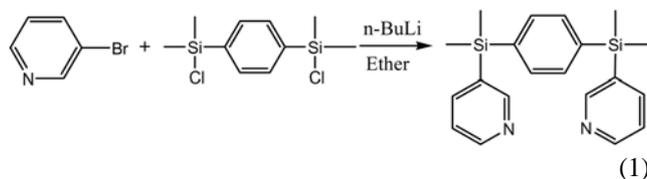
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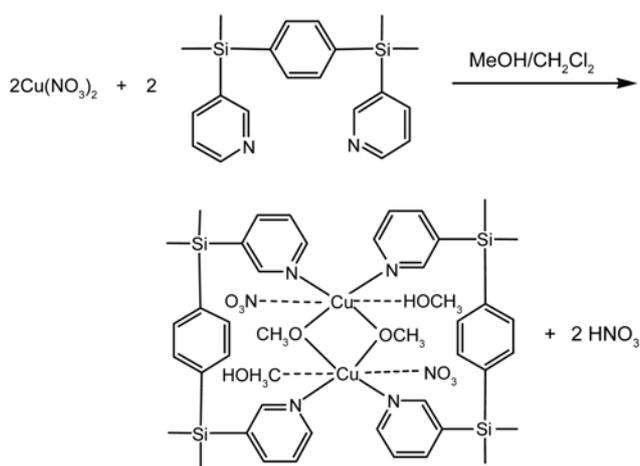
Elegant construction of metal coordination complexes with specific motifs is a thematic issue since the coordination materials have potential applications such as molecular separation, toxic materials adsorption, molecular containers, ion exchangers, molecular recognition, and luminescent sensors.¹⁻⁶ Thus, various kinds of framework molecules have been synthesized by the coordinations of metal ions with tailor-made organic tectonics⁷⁻¹⁰ even though serendipitous motifs have been frequently formed owing to the presence of unpredictable weak interactions such as hydrogen bonds, van der Waals forces, metal-metal interactions, and π - π interactions.⁷⁻¹⁸ The molecular structures of multidentate N-donor ligands including flexibility play key roles in the construction of the coordination materials. Recently, we have demonstrated that various silicon-containing pyridyl ligands are useful for the synthesis for desirable skeletal structures since the ligands are adjustable in their potential bridging ability and length, possess flexible angles around silicon, and are conformationally non-rigid.¹⁹⁻²³ On the other hand, dinuclear Cu(II) complexes have been a significant field owing to the following reasons: (i) they can be prepared by the normal methods using bridging ligands, (ii) they provide useful simple models for the study of the magnetic interaction of two unpaired *d* electrons, and (iii) they are useful models of the biological copper systems.²⁴ These factors have provided major incentives in the researches of novel dimeric copper(II) complexes. In order to expand the dimeric copper(II) chemistry, the slow diffusion of Cu(NO₃)₂ in methanol with 1,4-bis(dimethyl-3-pyridylsilyl)benzene in dichloromethane was accomplished. Herein, we report a doubly supported cyclodimeric copper(II) complex with methanol molecules as a sixth ligand.

The new ligand, 1,4-bis(dimethyl-3-pyridylsilyl)benzene (L), was prepared by the reaction of 1,4-bis(chlorodimethylsilyl)benzene with 3-bromopyridine according to the literature method (eq. 1).²⁵ The slow diffusion of Cu(NO₃)₂ in methanol into L in dichloromethane produced purple crystals suitable for X-ray crystallography as shown in Scheme 1. Even though the crystals have methanol molecules, they are very stable under an aerobic condition at room temperature. The product was insoluble in common organic solvents such as toluene, benzene, tetrahydrofuran, and acetone, but is

slightly soluble in methanol. The product seems to be dissociated in Me₂SO and N,N'-dimethylformamide. The formation of the product was not significantly affected by the change of reactant mole ratio and concentration, indicating that the compound is a favorable species.



X-ray characterization on a single crystal has provided a unique cyclodimeric species of the building block, [Cu(μ -OMe)(L)(NO₃)(MeOH)] (Scheme 1). The C₂ symmetric (perpendicular to the center of the Cu, O, Cu, and O plane) crystal structure of [Cu(μ -OCH₃)(L)(NO₃)(CH₃OH)]₂ is depicted in Figure 1 along with relevant bond distances and angles. Each copper(II) ion is a pseudo octahedral N₂O₄ coordination arrangement with a NO₃⁻ anion and a MeOH in a *trans* position (O-Cu-O = 176.2°) and two pyridine units and two bridged methoxy groups in a basal plane (Cu-N = 1.995(3) and 2.001(4) Å; Cu-O = 1.927(3) and 1.939(3) Å). A NO₃⁻ anion acts as a fifth ligand rather than a counter-anion (Cu...O(1) = 2.55 Å). Moreover, a methanol molecule



Scheme 1

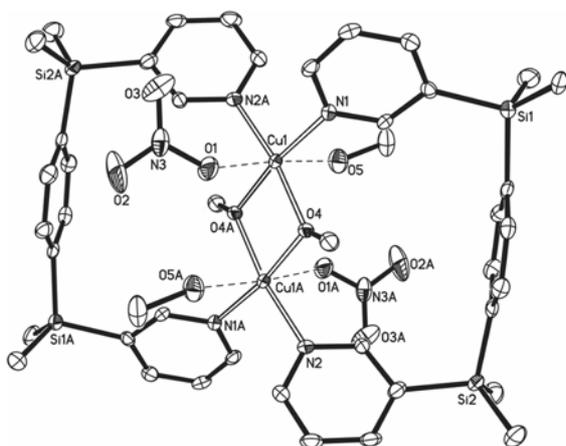
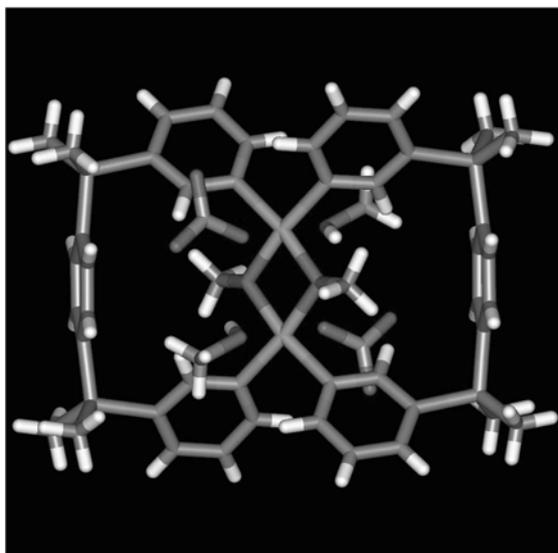


Figure 1. ORTEP drawing of $[\text{Cu}(\mu\text{-OCH}_3)(\text{L})(\text{NO}_3)(\text{CH}_3\text{OH})_2]$ showing the atomic labeling scheme and thermal ellipsoids at the 50% level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles ($^\circ$): Cu(1)-O(4), 1.927(3); Cu(1)-O(4)', 1.939(3); Cu(1)-N(2)', 1.995(3); Cu(1)-N(1), 2.001(4); Cu(1)-Cu(1)', 2.992(1); Si(1)-C(18), 1.852(5); Si(1)-C(17), 1.861(5); Si(1)-C(6), 1.874(4); Si(1)-C(4), 1.897(4); Si(2)-C(20), 1.863(5); Si(2)-C(9), 1.864(5); Si(2)-C(19), 1.866(5); Si(2)-C(12), 1.889(5); O(4)-Cu(1)-O(4)', 78.6(1); O(4)-Cu(1)-N(2)', 170.7(1); O(4)-Cu(1)-N(1), 93.1(1); O(4)-Cu(1)-N(1)', 94.5(1); O(4)-Cu(1)-N(1), 172.1(1); N(2)-Cu(1)-N(1)', 94.0(1); O(4)-Cu(1)-Cu(1)', 39.43(8); O(4)-Cu(1)-Cu(1)', 39.13(8); N(2)-Cu(1)-Cu(1)', 132.1(1); N(1)-Cu(1)-Cu(1)', 133.8(1); C(18)-Si(1)-C(17), 111.1(3).

is positioned as a sixth ligand ($\text{Cu}\cdots\text{O}(5) = 2.60 \text{ \AA}$) rather than simple solvate as will be explained in detail later. This interaction between Cu(II) ion and methanol molecule should contribute to the stability of the crystal. A significant feature is that an unprecedented cyclodimer is formed. The N-position of pyridyl group is an important factor in the formation of such a cyclodimer. In comparison, the reaction of $\text{Cu}(\text{ClO}_4)_2$ with *p*-pyridyl analogue ligand, 1,4-bis(dimethyl-4-pyridylsilyl)benzene, afforded the porous materials.²⁶ Of course, a subtle combination of the geometry of Cu(II) ion with the appropriate length, conformation, and steric effects of L is needless to say another important factor

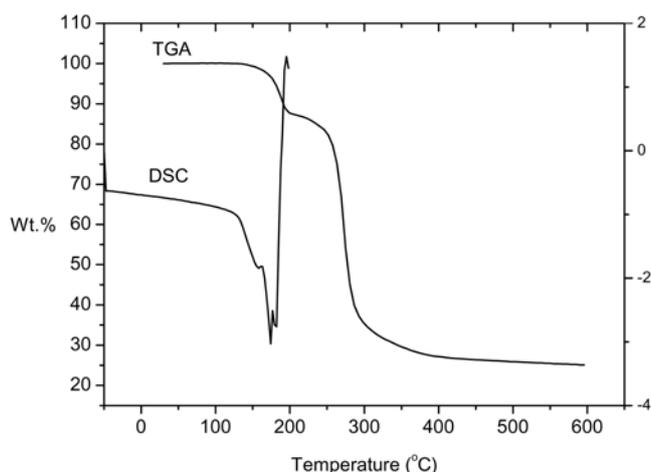


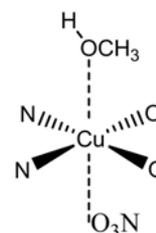
Figure 2. TGA and DSC curves of $[\text{Cu}(\mu\text{-OCH}_3)(\text{L})(\text{NO}_3)(\text{CH}_3\text{OH})_2]$.

for the formation of the doubly supported cyclodimeric species.

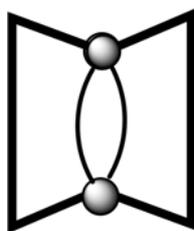
The thermogravimetric analysis (TGA) shows that the crystal has a thermal stability up to 150 °C even though the crystal has methanol molecules (Figure 2). An endothermic peak of the differential scanning calorimetric (DSC) curve was observed around 150–210 °C, indicating evaporation of the methanol ligand and μ -methoxide group. Actually, IR spectra of the crystalline sample before and after 180 °C still show nitrate peaks along with slightly color change. Thus, the TGA and DSC changes at the temperature range of 150–210 °C are apparently associated with the removal of methanol ligand and μ -methoxide group (calcd for methanol and methoxide group: 11.7%; obs: 12.0%). The product finally decomposes at the range of 250–300 °C, indicating the loss of L. The stable crystal at room temperature supports that the methanol molecule acts as a sixth ligand rather than a simple solvate. Furthermore, the pyridyl group containing a silicone moiety is a stronger Lewis base than a simple pyridine analogue. The strong donating ability may be partly responsible for the formation of stable complexes.

The structure of the present product is a doubly supported cyclodimer with a pseudo octahedral (N_2O_4) Cu(II) ion (Scheme 2). The coordination character results from the ligand field environment provided by the different donations including steric effects of L. A combination of appropriate length, N-position, and Lewis basicity of the ligand seems to construct the unique cyclodimer (Scheme 3).

In conclusion, the dinuclear copper(II) complex is an



Scheme 2



Scheme 3

unprecedented doubly-supported cyclodimer with methanol molecules as a sixth ligand. The *m*-pyridyl ligand containing a silicone moiety may be a valuable tectonic for the cyclodimeric structure. Further experiments will provide more detailed information on the enormous potentials such as catalytic properties, adsorption-desorption of small solvent molecules, and hydrophilicity.

Experimental

Preparation of 1,4-bis(dimethyl-3-pyridinylsilyl)benzene (L). To a solution of 3-bromopyridine (2.25 g, 14 mmol) in dry ethyl ether (40 mL) under nitrogen gas was added dropwise *n*-butyllithium (5.76 mL of 2.5 M solution in hexane, 14.4 mmol) at -79°C . The resulting mixture was stirred at the temperature for 1 h. 1,4-Bis(chlorodimethylsilyl)benzene (1.77 g, 6.4 mmol) was slowly added to the dark yellow suspension for 2 h at room temperature. Distilled water (20 mL) was added into the reaction solution, and the organic solution layer was separated. The organic solution was washed with water (2×20 mL), and then was dried over MgSO_4 . The crude product was purified by column chromatography on silica gel with ethyl acetate. The solvent was evaporated to obtain solid in 65% yield. mp 86°C . Anal. Calcd for $\text{C}_{20}\text{H}_{24}\text{N}_2\text{Si}_2$: C, 68.91; H, 6.94; N, 8.04. Found: C, 68.89; H, 6.91; N, 8.02. $^1\text{H NMR}$ (CDCl_3 , SiMe_4): 0.62 (s, 12H), 7.25 (m, 2H), 7.51 (s, 4H), 7.77 (m, 2H), 7.58 (m, 2H), 8.68 (s, 2H).

$[\text{Cu}(\mu\text{-OMe})(\text{L})(\text{NO}_3)(\text{MeOH})]_2$. A dichloromethane solution (2 mL) of L (17 mg, 0.05 mmol) was slowly diffused into a methanol solution (6 mL) of $\text{Cu}(\text{NO}_3)_2$ (9 mg, 0.025 mmol). Blue crystals formed at the interface, and were obtained in 12 days in 70% yield. Chemical analysis results are consistent with calculated values. m.p. 150°C (dec). IR (KBr, cm^{-1}): 3400 (br, O-H), 1591 (m), 1387 (s, NO_3), 1309 (s), 1254 (m), 1136 (m), 1039 (m), 804 (s), 777 (s), 709 (m), 511 (m).

Crystal data for $[\text{Cu}(\mu\text{-OMe})(\text{L})(\text{NO}_3)(\text{MeOH})]_2$: monoclinic, $P2_1/n$ $a = 9.3296(4) \text{ \AA}$, $b = 16.6558(7) \text{ \AA}$, $c = 16.7548(7) \text{ \AA}$, $\beta = 98.425(1)^{\circ}$, $V = 2575.5(2) \text{ \AA}^3$, $Z = 2$, $D_{\text{calc}} = 1.388 \text{ Mg m}^{-3}$, $F(000) = 1128$, $\lambda = 0.71073 \text{ \AA}$, $\mu = 0.978 \text{ mm}^{-1}$, crystal size $0.30 \times 0.30 \times 0.10 \text{ mm}^3$, $R(wR2) = 0.0535$ (0.1207) on 5260 unique reflections with $I > 2\sigma(I)$,

GOF = 1.020, 298 parameters refined. A Bruker SMART automatic diffractometer a CCD detector at ambient temperature; Sheldrick, G. M. SHELXS-97 and SHELXL-97: Programs for Structure Determination and Refinement; University of Göttingen, Germany, 1997.²⁷ The crystallographic data have been deposited with the Cambridge Crystallographic Data Centre CCDC (12 Union Road, Cambridge, CB2 1 EZ, UK) and are available on request by quoting the deposition number CCDC 642804.

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