**Cu(hfa)$_2$(µ-1,4-dicyanobenzene) and Cu(2,13-dioxoOEiBC)의 합성과 특성 분석**

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**Synthesis and Characterization of Cu(hfa)$_2$(µ-1,4-dicyanobenzene) and Cu(2,13-dioxoOEiBC)**

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Crystal engineering and the design of solid-state architectures have become an area of increasing interest over recent years. The packing of molecules into arrays of beautiful structures is the result of metal-ligand interactions$^{1-4}$ or noncovalent interactions (hydrogen bonding, π–π stacking, etc.$^{5,7}$ With this in mind, we were interested in monitoring 1) the formation of multidimensional networks and 2) the effect of ligand bulk on the π–π stacking interactions.$^{8,10}$ Herein, we describe the synthesis and characterization of two copper complexes, Cu(hfa)$_2$, (µ-1,4-dicyanobenzene) and Cu(2,13-dioxoOEiBC). The Cu(hfa)$_2$(µ-1,4-dicyanobenzene) shows one-dimensional chain, while Cu(2,13-dioxoOEiBC) shows no π–π stacking interaction.

**EXPERIMENTAL SECTION**

**General Information.** All manipulations were performed under an inert atmosphere using Schlenk techniques. All solvents were distilled by standard techniques. Hhfa(hexafluoropentanedione) and H$_2$OEP(octaethylporphyrin) were purchased from Aldrich Chemicals and used as received. UV/Vis/NIR electronic absorption spectra were obtained on a Perkin-Elmer UV/Vis/NIR Lambda 19 spectrophotometer. IR spectra were recorded as KBr pellets on a Perkin-Elmer 883 spectrometer.

**Synthesis of Cu(hfa)$_2$(µ-1,4-dicyanobenzene).** To a benzene solution of Cu(hfa)$_2$ (0.20 g, 0.42 mmol) was added 1,4-dicyanobenzene (0.054 g, 0.42 mmol). The resulting solution was refluxed for 24 h. After cooling to ambient temperature, the solution was filtered and volume of the filtrate was reduced to half. Slow evaporation of this solution gave green crystals suitable for X-ray crystallography. Yield: 0.22 g, 87%. mp 181-193 °C. IR (KBr, cm$^{-1}$): 3380 (br, m), 2210(m), 1625(s), 1550(m), 1525(m), 1390(m), 1245(s), 1220(s), 1140(s), 1095(m), 842(m), 795(s).

**Synthesis of Cu(2,13-dioxoOEiBC).** Synthesis of H$_2$(2,13-dioxoOEiBC), 3,3,7,8,12,12,17,18-octaethyl-(3H,12H)-porphine-2,13-dione, was based on the literature with modification.$^{11}$ The crude product was chromatographed into two fractions on a silica gel column (60-200 mesh). The first fraction was collected with dichloromethane/hexane (60:40
volume) until the eluent became green. The second fraction was eluted with dichloromethane. The second fraction was rechromatographed on a silica gel column using dichloromethane/hexane (70:30 volume). The last fraction, containing H$_2$(2,13-dioxoOEiBC), was collected. Yield: 5%. UV-vis(dichloromethane solution): $\lambda_{\text{max}}$ 398, 410, 514, 550, 654, 688 nm. Insertion of copper into the H$_2$(2,13-dioxoOEiBC) was accomplished by the reaction of free base and copper(II) acetate in DMF. The reaction product was chromatographed on a silica gel column (60-200 mesh) using dichloromethane/hexane (50:50 volume). Dark violet Cu(2,13-dioxoOEiBC) was eluted as a major product. UV-Vis(dichloromethane solution): $\lambda_{\text{max}}$ 403(soret), 600, 605 nm. IR(KBr): $\nu$ C=O 1712 cm$^{-1}$.

Oxidation of Cu(2,13-dioxoOEiBC) was carried out by the reaction of Cu(2,13-dioxoOEiBC) with tris(4-bromophenyl)aminium hexachloroantimonate. Cu(2,13-dioxoOEiBC) (25 mg, 0.040 mmol) and tris(4-bromophenyl)aminium hexachloroantimonate (34 mg, 0.042 mmol) were placed in a 100 mL Schlenk flask and dried for 1 h. After drying, dichloromethane was added to the Schlenk flask and the solution immediately turned brown. After stirring for 30 minutes, hexane was added to the solution. The mixture was filtered, and the brown solid was dried in vacuo; the yield was quantitative. UV-Vis (dichloromethane solution): $\lambda_{\text{max}}$ 385, 510, 590 nm. IR(KBr): $\nu$ C=O 1725 cm$^{-1}$.

RESULTS AND DISCUSSION

Cu(hfa)$_2$(µ-1,4-dicyanobenzene) was obtained by the reaction of Cu(hfa)$_2$ and 1,4-dicyanobenzene in benzene. Suitable crystals were harvested from the slow evaporation of the benzene solution.

Cu(hfa)$_2$(µ-1,4-dicyanobenzene) → polymeric Cu(hfa)$_2$(µ-1,4-dicyanobenzene)

The molecular structure of Cu(hfa)$_2$(µ-1,4-dicyanobenzene) is shown in Fig. 1, with the F atoms of hfa anionic ligands are omitted for clarity.\textsuperscript{12}

Copper atom binds to four oxygen atoms, contributed by two bidentate hfa anionic ligands, resulting in a square planar structure. The square planar Cu(hfa)$_2$ unit is bridged by 1,4-dicyanobenzene to give a linear structure. The extended one-dimensional polymeric structure of this compound.
The Cu-O bond distances fall into two distinctly different groups; Cu-O(1) and Cu-O(2), 1.911(9) Å and Cu-O(3) and Cu-O(4), 1.912(9) Å. The average Cu-N bond distance is 2.542(9) Å. The average ring O-Cu-O angle is 92.5(4)°. A comparison of bond distances and angles of Cu(hfa)$_2$($\mu$-1,4-dicyanobenzene) with those of other complexes containing Cu(hfa)$_2$ unit, Cu(hfa)$_2$ and Cu(hfa)$_2$(H$_2$NCH$_2$CH$_2$OH), is shown in Table 2. This reveals that the average Cu-O bond distance of the six-coordinated Cu(hfa)$_2$-(H$_2$NCH$_2$CH$_2$OH), 1.990(4) Å, is longer than in four-coordinated Cu(hfa)$_2$, compound, 1.911(7) Å. Interestingly, the molecular structure of Cu(hfa)$_2$-(μ-1,4-dicyanobenzene) shows two distinct types of Cu-O bond distance, short distance with one hfa ligand and longer distance with the other hfa ligand. The average Cu-N distance in Cu(hfa)$_2$-(μ-1,4-dicyanobenzene), 2.542(9) Å, is longer than in Cu(hfa)$_2$-(H$_2$NCH$_2$CH$_2$OH), 2.003(3) Å, indicating a Jahn-Teller elongation along N(1)-Cu-N(2) vector. The thermogravimetric behaviors of the complex have been investigated by thermogravimetry (TGA) over the temperature range 30-450 °C. Atmospheric pressure thermogravimetric analysis of Cu(hfa)$_2$-(μ-1,4-dicyanobenzene) reveals that weight loss takes place in the 100-190 °C temperature range and shows that no weight loss after 200 °C.

The final residual weight (11%) agrees with the composition of CuO(12%). Cu(hfa)$_2$, has been used for the chemical vapour deposition(CVD) of copper films. The TGA analysis indicates that Cu(hfa)$_2$-(μ-1,4-dicyanobenzene) can not be used as a CVD precursor.

Cu(2,13-dioxoOEiBC) was obtained by the reaction of Cu(OAc)$_2$, and H$_2$(2,13-dioxoOEiBC) in DMF.
The oxidation of Cu(2,13-dioxoOEiBC) with tris(4-
bromophenyl)ammonium hexachloroantimonate results in
the formation of the π-cation radical, [Cu(2,13-
dioxoOEiBC)][SbCl6].

\[
\text{Cu(OAc)}_2 + \text{H}_{2}(2,13\text{-dioxoOEiBC}) \\
\rightarrow \text{Cu}(2,13\text{-dioxoOEiBC}) \\
\text{Cu}(2,13\text{-dioxoOEiBC}) + \text{oxidant} \\
\rightarrow [\text{Cu}(2,13\text{-dioxoOEiBC})]^+ 
\]

The electronic spectra of [Cu(2,13-dioxoOEiBC)]+ have a blue-shifted and broadened Soret band and
π-π aggregation bands at 1285 and 1548 nm. 
Near-IR bands for [Cu(oxoOEC·)]+ show no
π-π aggregation due to the bulky peripheral substituents.

Metallo-oxooctaethylchlorin show near-IR bands.

π-π aggregation is observed in the region of 900-3000 nm at the
highest concentration we were able to use. This
observation suggests that the [Cu(2,13-dioxoOEiBC)]+
radical is monomeric because the increased
number of peripheral substituents prevents aggregation of the molecule. This phenomenon is also
found in [Cu(TPP)]+ and [Cu(TMPC)]+ radicals. The solid-state structures of [Cu(TPP)]+ and [Cu(TMPC)]+
show no π-π π-π aggregation due to the bulky peripheral substituents.

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P1-bar, a=8.129(1), b=8.322(1), c=9.079(1) Å, α=95.19(1), 
β=97.86(1), γ=97.86(1), V=572.21(1)Å3. The structure 
was solved by a heavy atom method and refined to R1 
=0.044 and wR2=0.115 against 1930 observed 
[I>2σ(I)].
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14. TGA analysis was carried out on a SETARAM TGA- 
92 instrument. The weight of sample was between 10 and 
25 mg. The measurement was performed in alumina 
crucibles under an atmosphere of flowing dry nitrogen, 
using heating rates of 5 °C/min.
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17. Abbreviations used in this paper include: 2,13-dioxoOEiBC, 
3,3,7,8,12,17,18-octaethyl-(3H,12H)-porphine-2,13-
dionato(2-); hfa, anion of hexafluoropentanedione; H2OEP,

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octaethylporphyrin; H\textsubscript{2}oxoOEC, oxooctaethylchlorin; DMF, N,N-dimethylformamide; TMP, dianion of tetramethylporphyrin; TPP, dianion of tetraphenylporphyrin.