

RESEARCH ARTICLE

Dinuclear Copper(II) 3,4,5-Tri-*O*-benzylgallate

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Abstract:

Background:

Ellagitannins have attracted much attention because of the biological and pharmacological activities. In the total synthesis of ellagitannins, 3,4,5-tri-*O*-benzylgallic acid has been a key compound to introduce the protected galloyl group. From the perspective of coordination chemistry, 3,4,5-tri-*O*-benzylgallic acid is an interesting carboxylate ligand which might be capable of dinuclear carboxylate complex. Such a dinuclear carboxylate complex might be interesting as a new example of copper acetate type complexes.

Objectives:

The objective of the work is to synthesize a copper acetate type complex by using 3,4,5-tri-*O*-benzylgallic acid and to see a new feature of copper acetate compounds, by elucidating the crystal structure, magnetic property, and adsorption property for N₂ gas.

Methods:

Copper(II) 3,4,5-tri-*O*-benzylgallate has been synthesized by a reaction of 3,4,5-tri-*O*-benzylgallic acid and copper(II) nitrate at pH=9 condition. The isolated complex was characterized using single-crystal X-ray structure analysis, XRD analysis, UV-visible spectroscopy, IR spectroscopy, and temperature dependence of magnetic susceptibility.

Results:

The crystal structure shows a crystallographically centrosymmetric dinuclear molecule with four carboxylato-bridges and axial dimethylformamide molecules and crystal dmf molecules [Cu...Cu 2.6345(12) Å]. In the crystal, 1D supramolecular assembly by π - π interaction between the benzyl aromatic rings of dinuclear molecules was observed. Temperature dependence of magnetic susceptibilities showed a considerable antiferromagnetic interaction between the two copper(II) ions ($2J = -214 \text{ cm}^{-1}$). Type-II gas-adsorption property was observed for N₂.

Conclusion:

A key-compound for the total synthesis of ellagitannins, 3,4,5-tri-*O*-benzylgallic acid (Htbnng), was shown to be a new ligand for the synthesis of dinuclear copper acetate analogue with a lantern-type core, extending the realm of copper acetate clusters.

Keywords: Copper acetate, Crystal structure, Magnetic property, 3,4,5-Tri-*O*-benzylgallic Acid, Ellagitannins, Magnetic susceptibility.

Article History

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1. INTRODUCTION

Ellagitannins are a class of tannins containing galloyl and hexahydroxydiphenoyl groups, in which more than 1000 analogues have been found in natural systems [1]. These tannins have attracted much attention for a long period,

because they have interesting biological and pharmacological activities. So far, total synthesis has been attempted for more than 20 ellagitannins. The benzyl group was often used as an effective protecting group of the phenol groups in the total syntheses [2, 3], where 3,4,5-tri-*O*-benzylgallic acid (Fig. 1) is a key compound to introduce the protected galloyl group. From the perspective of coordination chemistry, 3,4,5-tri-*O*-benzylgallic acid is an interesting carboxylate ligand which might be capable of dinuclear carboxylate complex. Such a dinuclear carboxylate complex might be interesting as a new example of copper acetate. Copper acetate is one of the oldest metal complexes with a unique Cu_2 cluster and has attracted much attention since the discovery of the lantern-like acetato-bridged cluster and antiferromagnetic spin-coupling [4 - 13]. Recently, a unique di- μ -acetato-bridged dinuclear cluster, $[\text{Cu}_2(\text{CH}_3\text{CO}_2)_4(\text{EtimH})_2]$ (EtimH = 2-ethylimidazole), was reported by Hernandez *et al.* [14]. They aimed to attempt to form porous copper acetate-2-ethylimidazole. We have been engaged in the synthesis of copper acetate analogues and their metal-assembled complexes [13, 15 - 31]. During the course of our studies, we found that copper(II) benzoate forms a chain compound with pyrazine and the assembled chain complex has a porous structure and an adsorption property for N_2 , where the aromatic benzoate groups form a hydrophobic micropore [19, 30]. This is another interesting feature of copper acetate analogues. In this study, we synthesized a new copper acetate analogue by the reaction of 3,4,5-tri-*O*-benzylgallic acid (abbreviated as Htbng) with a copper(II) salt. The bulky aromatic groups of tbng⁻ ligand may be expected to form enough space for gas adsorption property in the copper carboxylate.

2. MATERIALS AND METHODS

All the chemicals except for the Htbng ligand were commercial products and were used as supplied. Elemental analyses for C, H, and N were performed using a Thermo-Finnigan FLASH EA1112 series CHNO-S analyzer. Infrared spectra were measured with a JASCO MFT-2000 FT-IR Spectrophotometer in the 4000-600 cm^{-1} region. Diffused reflectance spectrum was measured with a Shimadzu UV-vis-NIR Recording Spectrophotometer Model UV-3100 in the 200-1500 nm region. Magnetic susceptibilities were measured with a Quantum Design MPMS-XL7 SQUID susceptometer over a temperature range of 4.5-300 K. Powder X-ray Diffraction (PXRD) data were collected in the θ range of 5-40° on a RIGAKU RINT2000/PC diffractometer with Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$). Adsorption measurement for N_2 was performed by a MicrotracBEL BELSORP-mini II. Prior to the adsorption, the sample was evacuated at 298 K for 2h.

2.1. Synthetic Procedures

The Htbng ligand was synthesized according to the previously reported method [32]. Copper(II) carboxylate was synthesized by the following method. $[\text{Cu}_2(\text{tbng})_4(\text{dmf})_2] \cdot \text{H}_2\text{O}$: A 0.198 g (0.45 mmol) portion of Htbng and 10 cm^3 of methanol were added to a 6 cm^3 of 0.10 M sodium hydroxide solution. The mixed solution was adjusted to pH = 9 by adding a small amount of nitric acid. To this solution, a solution of copper(II) nitrate trihydrate (0.0618 g, 0.25 mmol) in water (3 cm^3) was added with stirring to give a yellowish-green precipitate. The precipitate was collected and dried under

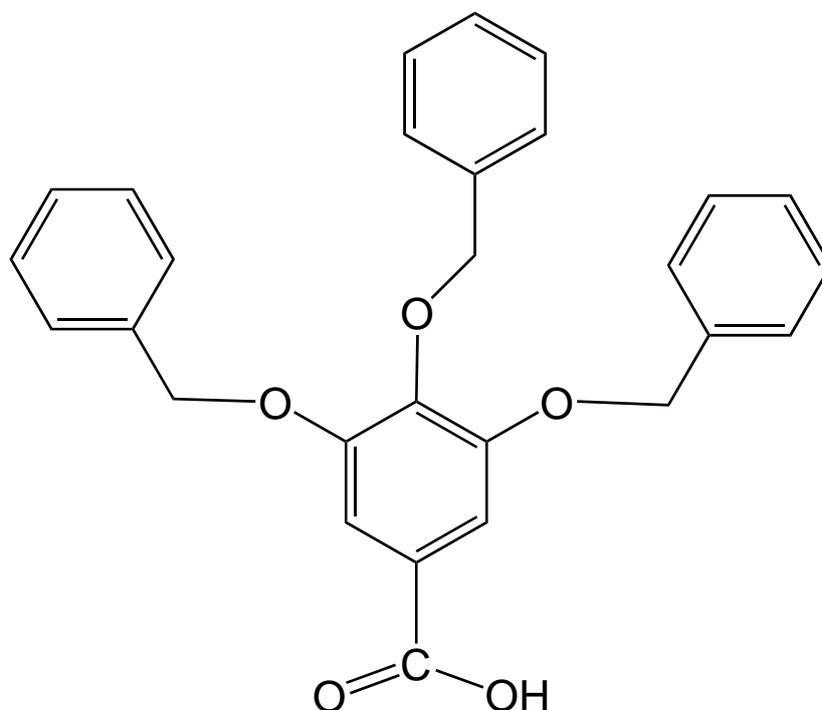


Fig. (1). 3,4,5-Tri-*O*-benzylgallic acid, Htbng.

vacuum. Yield, 0.204 g (85% based on the metal salt). Anal. Found: C, 68.93; H, 5.42%. Calcd for $C_{112}H_{100}Cu_2O_{24}$ ($Cu_2(tbng)_4 \cdot 4H_2O$): C, 68.74; H, 5.15%. The precipitate was recrystallized from dmf-methanol to give green crystals. Anal. Found: C, 69.03; H, 4.96; N, 1.55%. Calcd for $C_{118}H_{108}Cu_2N_2O_{23}$ ($[Cu_2(tbng)_4(dmf)_2] \cdot H_2O$): C, 69.16; H, 5.31; N, 1.37%. IR (KBr, cm^{-1}): 3083, 3061, 3030 (ν (aromatic)H), 2924 ($\nu_{as}CH_2$), 2860 (ν_sCH_2), 1577 ($\nu_{as}COO$), 1407 (ν_sCOO). Diffuse reflectance spectra: λ_{max} 272, 293, 298, 375sh, 716 nm.

Table 1. Crystal and experimental data.

Chemical formula: $C_{130}H_{134}Cu_2N_6O_{26}$
Formula weight = 2323.57
$T = 100$ K
Crystal system: triclinic Space group: P
$a = 10.430(3)$ Å $\alpha = 109.406(4)^\circ$
$b = 15.847(5)$ Å $\beta = 92.717(4)^\circ$
$c = 19.990(6)$ Å $\gamma = 108.669(4)^\circ$
$V = 2908.3(16)$ Å ³ $Z = 1$
$D_x = 1.327$ g/cm ³
Radiation: Mo $K\alpha$ ($\lambda = 0.71073$ Å)
μ (Mo $K\alpha$) = 0.444 mm ⁻¹ $F(000) = 1222$
Crystal size = $0.12 \times 0.08 \times 0.03$ mm ³
No. of reflections collected = 13796
No. of independent reflections = 9988
θ range for data collection: 1.10 to 25.02°
Data/Restraints/Parameters = 9988/0/745
Goodness-of-fit on $F^2 = 0.985$
R indices [$>2\sigma(I)$]: $R1 = 0.0673$, $wR2 = 0.1605$
R indices (all data): $R1 = 0.0949$, $wR2 = 0.1770$
$(\Delta/\sigma)_{max} = 0.000$
$(\Delta\rho)_{max} = 1.087$ eÅ ⁻³ $(\Delta\rho)_{min} = -0.642$ eÅ ⁻³
Measurement: Bruker Smart APEX-II ULTRA diffractometer
Program system: SHELXTL
Structure determination: Direct methods (SHELXS-97)
Refinement: full matrix least-squares (SHELXL-97)
CCDC deposition number: 1815964

2.2. Crystallography

Single-crystals suitable for X-ray analysis were obtained due to very few amount of small crystals by slow diffusion of a dmf solution of $[Cu_2(tbng)_4(dmf)_2] \cdot H_2O$. Single-crystal diffraction data were measured on a Bruker Smart APEX-II ULTRA diffractometer equipped with a multilayered confocal mirror monochromator and a Mo-K α radiation source ($\lambda = 0.71073$ Å). Crystal data and details concerning data collection are given in Table 1. The structure was solved by direct methods, and refined by full-matrix least-squares methods. The hydrogen atoms were inserted at their calculated positions and fixed there. All of the calculations were carried out utilizing the SHELXTL software package [33]. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre:

Deposit number CCDC-1815964. 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).

3. RESULTS AND DISCUSSIONS

Elemental analysis data of the isolated compound are in accordance with the formulation $[Cu_2(tbng)_4(dmf)_2] \cdot H_2O$. IR data showed two COO stretching bands at 1577 and 1407 cm^{-1} with the difference in energy characteristic of *syn-syn*-bridging carboxylate [34]. As shown in Fig. (2), the diffuse reflectance spectrum of $[Cu_2(tbng)_4(dmf)_2] \cdot H_2O$ shows strong bands at 272, 293, and 298 nm, and a shoulder at 370 nm in the UV region, and a broad band at 716 nm with a shoulder at lower energy side in the vis-NIR region. The former four bands can be assigned to LMCT bands from the carboxylato-oxygen to the Cu^{II} d orbital. The vis-NIR region band can be associated with d-d transitions, confirming a square-pyramidal coordination environment of the copper(II) atoms [35].

The molecular structure for $[Cu_2(tbng)_4(dmf)_2] \cdot 4dmf$ was drawn as an ORTEP diagram in Fig. (3). The asymmetric unit contains two crystal dmf molecules and one-half of dinuclear $[Cu_2(tbng)_4(dmf)_2]$ unit with a crystallographic inversion center at the midpoint of the Cu1 and Cu1' atoms. The dinuclear unit has a lantern-like dinuclear core bridged by four $tbng^-$ ligands in a *syn-syn* fashion [13]. The Cu1...Cu1' distance is 2.6345(12) Å, which is in the range found in dinuclear copper(II) carboxylates [6 - 13]. The coordination geometry around each copper atom is an elongated square-pyramid. The bond distances of the Cu1 and basal O atoms are 1.957(3)-1.977(3) Å, which are within the normal range found in copper(II) carboxylates [6 - 13]. The fifth position of the Cu1 atom is occupied by a DMF molecule with the Cu1-O11 distance of 2.166(3) Å, which is also in the normal range as axial bonding for the copper(II) carboxylates [6 - 13]. In the crystal, DMF molecules are trapped into the small space between the dinuclear units (Fig. 4). Each dinuclear molecule is associated with $\pi \cdots \pi$ interaction of one of the three benzyl aromatic rings to form one-dimensional chain supramolecular network as shown in Fig. (5).

The magnetic data of $[Cu_2(tbng)_4(dmf)_2] \cdot H_2O$ are shown in the form of $\chi_A T$ vs. T plot in Fig. (6). The $\chi_A T$ value is 0.341 $cm^3 mol^{-1} K$ (per Cu^{II} unit) at 300 K. This corresponds to the magnetic moment of 1.65 μ_B , which is lower than the spin-only value (1.73 μ_B) as Cu^{II} (d^9 , $S = 1/2$) ion. The $\chi_A T$ decreases with lowering of the temperature and reaches value of 0.0046 $cm^3 mol^{-1} K$ at 4.5 K, showing an antiferromagnetic interaction between the two copper(II) ions. The magnetic data were analyzed by the Bleaney-Bowers equation based on the Heisenberg model ($H = -2JS_1 \cdot S_2$ ($S_1 = S_2 = 1/2$)) [5]:

$$\chi_A = (1-p)[Ng^2\mu_B^2/kT][3+\exp(-2J/kT)]^{-1} + pNg^2\mu_B^2/4kT + Na,$$

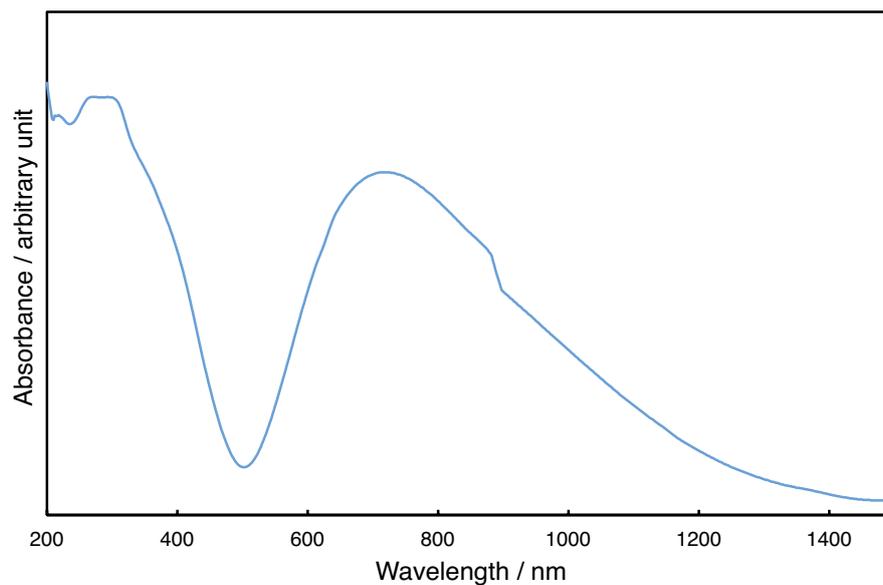


Fig. (2). Diffused reflectance spectrum of $[\text{Cu}_2(\text{tbng})_4(\text{dmf})_2] \cdot \text{H}_2\text{O}$.

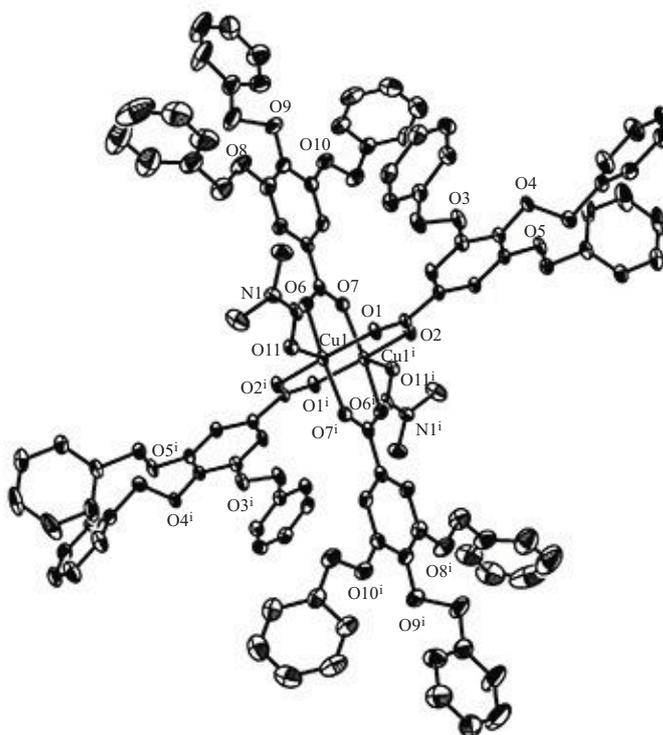


Fig. (3). ORTEP diagram of the dinuclear molecule of $[\text{Cu}_2(\text{tbng})_4(\text{dmf})_2] \cdot 4\text{dmf}$ with atom labeling. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°). $\text{Cu} \cdots \text{Cu}^i$ 2.6345(12), Cu1-O1 1.977(3), Cu1-O2^i 1.964(3), Cu1-O6 1.957(3), Cu1-O7^i 1.957(3), Cu1-O11 2.166(3); O1-Cu1-O2^i 168.95(11), O1-Cu1-O6 87.31(12), O1-Cu1-O7^i 92.52(12), $\text{O2}^i\text{-Cu1-O6}$ 90.56(12), $\text{O2}^i\text{-Cu1-O7}^i$ 87.38(12), O6-Cu1-O7^i 168.34(12), O11-Cu1-O1 91.02(11), O11-Cu1-O6 92.44(12), O11-Cu1-O2^i 99.90(11), O11-Cu1-O7^i 99.22(12). Symmetry code (i): $(-x, -y, -z)$.

Where J is an exchange coupling constant for the two copper(II) ions, p is the fraction of mononuclear impurity, and $N\alpha$ is the temperature-independent paramagnetism, which was set to $60 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for each copper(II) ion [8, 25, 30].

The best-fitting parameters were $2J = -214 \text{ cm}^{-1}$, $g = 2.13$, $p = 0.07$, showing an antiferromagnetic coupling between the two copper(II) ions. The $-2J$ value is a little smaller than those of copper(II) acetate ($\sim 284 \text{ cm}^{-1}$) [6] and most of copper(II)

benzoates ($-2J = 316\text{--}350\text{ cm}^{-1}$) [10], showing a relatively weak antiferromagnetic coupling. It is known that the larger bending angle of the OCO moiety of the benzoate group relative to the Cu-O \cdots O-Cu plane of the carboxylate-bridge, ϕ_{bend} , plays an important role to weaken the antiferromagnetic coupling *via* the benzoate bridges [10]. In the case of the most related copper(II) benzoate with 3,4,5-trimethoxybenzoate, $[\text{Cu}_2\{3,4,5\text{-}[(\text{CH}_3\text{O})_3\text{C}_6\text{H}_2\text{CO}_2]\}_4(\text{CH}_3\text{OH})_2]\cdot 2\text{dmf}$, the ϕ_{bend}

values are 2.8 and 2.9° , and shows a stronger antiferromagnetic interaction between the two copper(II) ions ($2J = -292\text{ cm}^{-1}$) [31]. The crystal structure of the present complex revealed that the benzoate group has a considerable bending with $\phi_{\text{bend}} = 9.4$ and 5.9° possibly because of the packing effect of the dinuclear clusters with bulky galloyl groups, resulting in a weaker antiferromagnetic coupling between the two copper(II) ions.

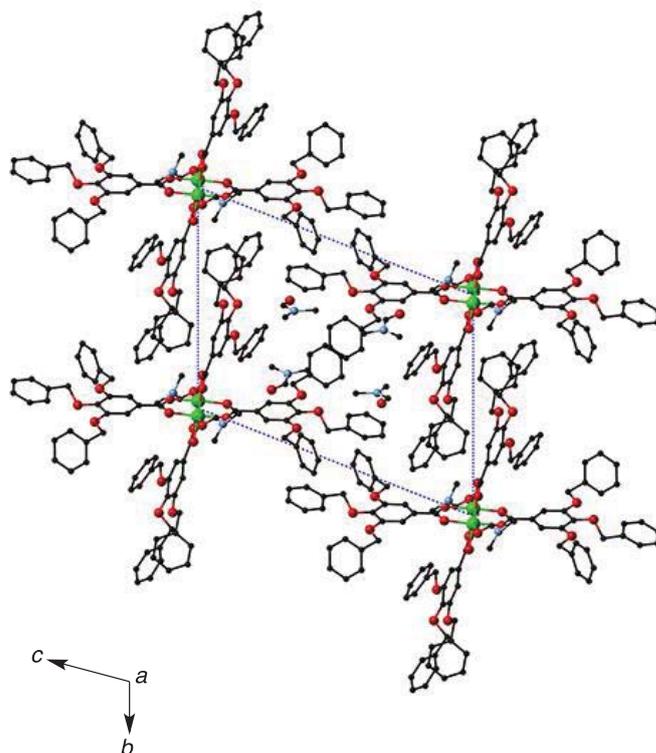


Fig. (4). Packing diagram of $[\text{Cu}_2(\text{tbng})_4(\text{dmf})_2]\cdot 4\text{dmf}$.

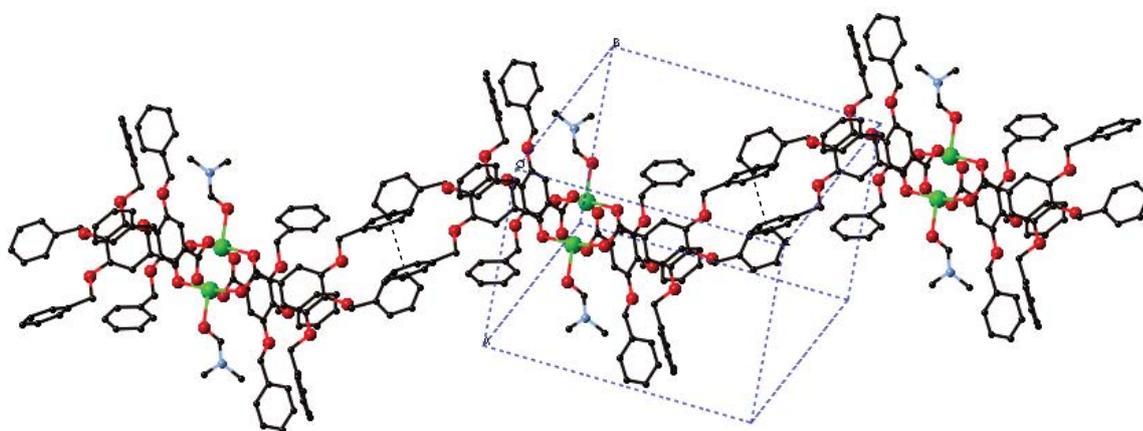


Fig. (5). View of the 1D supramolecular assembly of $[\text{Cu}_2(\text{tbng})_4(\text{dmf})_2]\cdot 4\text{dmf}$, showing $\pi\text{-}\pi$ interaction between the benzyl aromatic rings of dinuclear $\text{Cu}_2(\text{tbng})_4(\text{dmf})_2$ molecules by dashed lines.

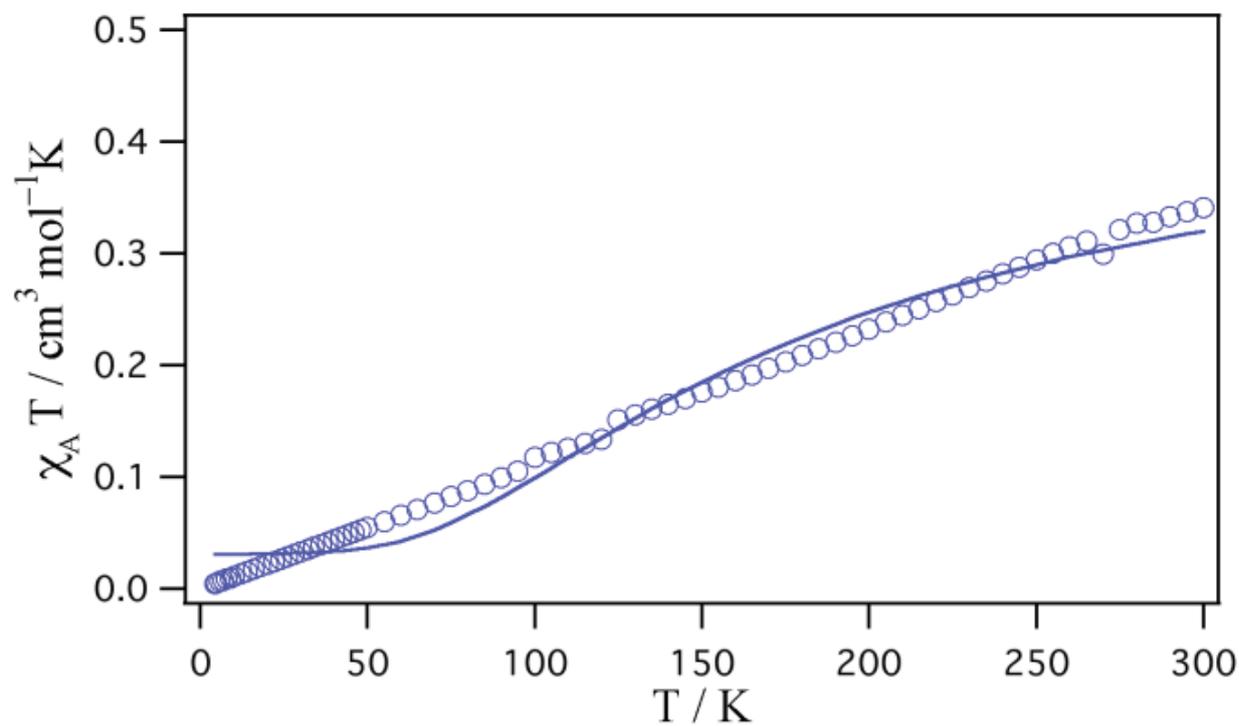


Fig. (6). Temperature dependence of $\chi_A T$ of $[\text{Cu}_2(\text{tbng})_4(\text{dmef})_2] \cdot \text{H}_2\text{O}$. The solid line represents the best fit of the data.

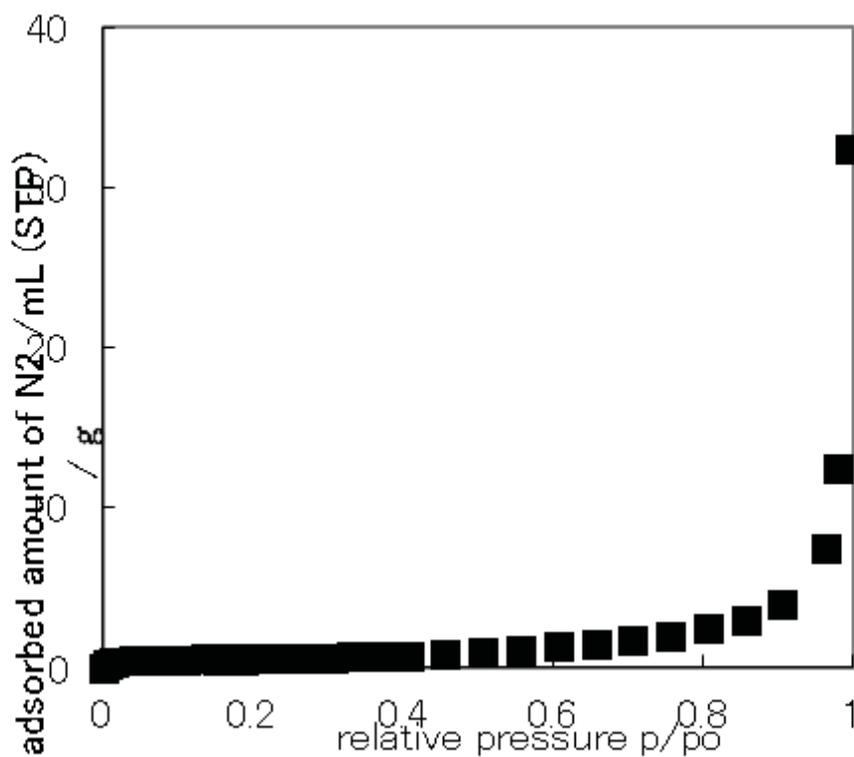


Fig. (7). N₂ adsorption isotherm of $[\text{Cu}_2(\text{tbng})_4(\text{dmef})_2] \cdot \text{H}_2\text{O}$.

The crystal structure of $[\text{Cu}_2(\text{tbng})_4(\text{dmf})_2] \cdot 4\text{dmf}$ did not show large voids, although it has many small cavities. The PXRD data of $[\text{Cu}_2(\text{tbng})_4(\text{dmf})_2] \cdot \text{H}_2\text{O}$ did not coincide with the simulated data from the crystal structure of $[\text{Cu}_2(\text{tbng})_4(\text{dmf})_2] \cdot 4\text{dmf}$, suggesting that the packing of the dinuclear molecules was influenced by the incorporation of the solvent. Therefore, we expected an adsorbing property for the present complex, if the bulky galloyl groups work well for porous structure. However, the adsorption isotherm on $[\text{Cu}_2(\text{tbng})_4(\text{dmf})_2] \cdot \text{H}_2\text{O}$ showed that the isotherm belongs to Type II in the IUPAC classification ($S_{\text{BET}} = 2.0 \text{ m}^2 \text{ g}^{-1}$) as shown in Fig. (7), suggesting the crystals to be non-porous. This is similar to the case for $[\text{Cu}_2\{3,4,5-(\text{CH}_3\text{O})_3\text{C}_6\text{H}_2\text{CO}_2\}_4(\text{CH}_3\text{OH})_2] \cdot 2\text{dmf}$ [31].

CONCLUSION

A key-compound for the total synthesis of ellagitannins, 3,4,5-tri-*O*-benzylgallic acid (Htbng), was shown to be a new ligand for the synthesis of dinuclear copper acetate analogue with a lantern-type core, extending the realm of copper acetate clusters.

CONSENT FOR PUBLICATION

Not applicable.

CONFLICT OF INTEREST

The authors declare no conflict of interest, financial or otherwise.

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