



## SYNTHESIS, CRYSTAL STRUCTURE, MAGNETIC PROPERTY, AND N<sub>2</sub>-GAS-ADSORPTION PROPERTY OF DINUCLEAR COPPER(II) 3,4,5-TRIMETHOXYBENZOATE

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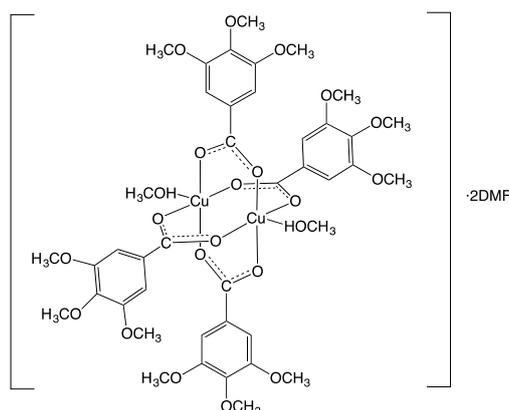
**Abstract:** Copper(II) 3,4,5-trimethoxybenzoate,  $[\text{Cu}_2(3,4,5\text{-(CH}_3\text{O)}_3\text{C}_6\text{H}_2\text{CO}_2)_4(\text{CH}_3\text{OH})_2] \cdot 2\text{DMF}$ , was prepared and characterized by elemental analysis, infrared and UV-vis spectra and temperature dependence of magnetic susceptibilities (4.5–300 K). The crystal structure was determined by the single-crystal X-ray diffraction method. It crystallizes in the triclinic space group  $P\bar{1}$  with  $a = 8.2110(13) \text{ \AA}$ ,  $b = 13.181(2) \text{ \AA}$ ,  $c = 13.409(2) \text{ \AA}$ ,  $\alpha = 97.967(3)^\circ$ ,  $\beta = 102.378(3)^\circ$ ,  $\gamma = 105.009(3)^\circ$ ,  $V = 1339.8(4) \text{ \AA}^3$ ,  $D_x = 1.465 \text{ g/cm}^3$ , and  $Z = 1$ . The  $R1 [I > 2\sigma(I)]$  and  $wR2$  (all data) values are 0.0363 and 0.0816, respectively, for all 5991 independent reflections. The crystal contains crystallographically centrosymmetric dinuclear molecule with axial methanol molecules and crystal DMF molecules [ $\text{Cu} \cdots \text{Cu}$  2.6190(6)  $\text{ \AA}$ ]. Magnetic susceptibility data show a considerable antiferromagnetic interaction between the two copper(II) ions ( $2J = -292 \text{ cm}^{-1}$ ). Gas-adsorption behavior was investigated for N<sub>2</sub>.

**Keywords:** Dinuclear copper complex, crystal structure determinations, nitrogen gas absorption property.

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## INTRODUCTION



**Figure 1:** Chemical structure of  $[\text{Cu}_2(345\text{tmbz})_4(\text{CH}_3\text{OH})_2] \cdot 2\text{DMF}$ .

Copper acetate  $[\text{Cu}_2(\text{CH}_3\text{CO}_2)_4(\text{H}_2\text{O})_2]$  is a famous copper(II) compound with a lantern-like dinuclear core and has attracted much attention for a long period because of the unique structure and properties [Horikoshi and Mikuriya, 2005; Matsushima *et al.*, 1999; Mori *et al.*, 1999; Mikuriya *et al.*, 1995; Mikuriya *et al.*, 1977; Mikuriya *et al.*, 1999; Mikuriya *et al.*, 2000a; Mikuriya *et al.*, 2000b; Mikuriya *et al.*, 2002a; Mikuriya *et al.*, 2002b; Mikuriya, 2008; Mikuriya *et al.*, 2015a; Mikuriya *et al.*, 2015b, Nakashima *et al.*, 1985; Nukada *et al.*, 1999; Nukada *et al.*, 2001; Nukada *et al.*, 2015]. There are a number of analogous compounds with a lantern-like core as dinuclear metal carboxylates [Cotton *et al.*, 2005]. Previously, we reported that copper(II) benzoate forms a chain compound with pyrazine and the assembled compound has a gas-occlusion property for  $\text{N}_2$  [Nukada *et al.*, 1999]. We found that the aromaticity of the benzoate group plays an important role to construct a hydrophobic micropore [Nukada *et al.*, 2015]. In order to understand the adsorption properties of these compounds, systematic investigations are needed for various types of copper(II) carboxylates. In this study, we synthesized a dinuclear copper(II) complex with a lantern-like core by using 3,4,5-trimethoxybenzoic acid (H345tmbz) substituted with methoxy group at the three positions of the benzoate group (Figure 1) in order to give variety to these compounds. The isolated compound was characterized by measuring elemental-analysis data, infrared and UV-Vis spectra, and temperature dependence of magnetic susceptibility. Crystal structure was determined by the single-crystal X-ray diffraction method. Gas-adsorption behavior was investigated for  $\text{N}_2$ .

## EXPERIMENTAL

Copper(II) 3,4,5-trimethoxybenzoate was prepared by the following method.  $[\text{Cu}_2(345\text{tmbz})_4(\text{CH}_3\text{OH})_2] \cdot 2\text{DMF}$ : A 0.505 g (2.38 mmol) portion of 3,4,5-trimethoxybenzoic acid was added to a 5  $\text{cm}^3$  of 0.10 M sodium hydroxide solution. The mixed solution was neutralized by adding nitric acid with phenolphthalein indicator. To this solution, a solution of

copper(II) nitrate trihydrate (0.301 g, 1.25 mmol) in water (5 cm<sup>3</sup>) was added with stirring to give a pale blue precipitate. The precipitate was collected and dried under vacuum. Yield, 0.587 g (72.2%). Anal. Found: C, 47.57; H, 4.86%. Calcd for C<sub>40</sub>H<sub>48</sub>Cu<sub>2</sub>O<sub>22</sub>: C, 47.67; H, 4.80%. The precipitate was recrystallized from DMF-methanol to give greenish blue crystals. Anal. Found: C, 49.13; H, 5.39; N, 2.59%. Calcd for C<sub>48</sub>H<sub>66</sub>Cu<sub>2</sub>N<sub>2</sub>O<sub>24</sub>: C, 48.77; H, 5.63; N, 2.37%. IR (KBr, cm<sup>-1</sup>): 3019, 2943 ( $\nu_{\text{as}}\text{CH}_3$ ), 2838 ( $\nu_{\text{s}}\text{CH}_3$ ), 1574 ( $\nu_{\text{as}}\text{COO}$ ), 1415 ( $\nu_{\text{s}}\text{COO}$ ). Diffuse reflectance spectra:  $\lambda_{\text{max}}$  280, 370sh, 716 nm.

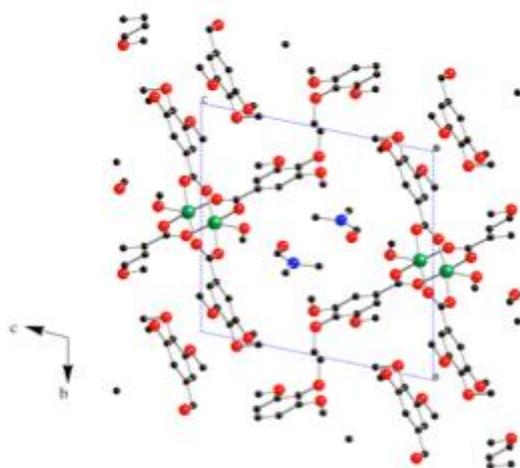
Measurements: Elemental analyses for C, H, and N were performed using a Thermo-Finnigan FLASH EA1112 series CHNO-S analyzer. Infrared spectra were measured with a JASCO MFT-2000 FT-IR Spectrometer in the 4000–600 cm<sup>-1</sup> region. Diffuse reflectance spectra were measured with a Shimadzu UV-vis-NIR Recording Spectrophotometer Model UV-3100. Magnetic susceptibilities were measured with a Quantum Design MPMS-XL7 SQUID susceptometer operating at a magnetic field of 0.5 T over a range of 4.5–300 K. Adsorption measurements for N<sub>2</sub> were performed by a MicrotracBEL BELSORP-mini II. Prior to the adsorption, the sample was evacuated at 298 K for 2h.

X-Ray Crystallography: X-Ray diffraction data were collected on a Bruker CCD X-ray diffractometer (SMART APEX) using graphite-monochromated Mo-K $\alpha$  radiation. Crystal data of [Cu<sub>2</sub>(345tmbz)<sub>4</sub>(CH<sub>3</sub>OH)<sub>2</sub>] $\cdot$ 2DMF: C<sub>48</sub>H<sub>66</sub>Cu<sub>2</sub>N<sub>2</sub>O<sub>24</sub>,  $M_r = 1182.1$ ,  $T = 90$  K, triclinic, space group  $P\bar{1}$  with  $a = 8.2110(13)$  Å,  $b = 13.181(2)$  Å,  $c = 13.409(2)$  Å,  $\alpha = 97.967(3)^\circ$ ,  $\beta = 102.378(3)^\circ$ ,  $\gamma = 105.009(3)^\circ$ ,  $V = 1339.8(4)$  Å<sup>3</sup>,  $D_x = 1.465$  g/cm<sup>3</sup>, and  $Z = 1$ . The  $R_1 [I > 2\sigma(I)]$  and  $wR_2$  (all data) values are 0.0363 and 0.0816, respectively, for all 5991 independent reflections.

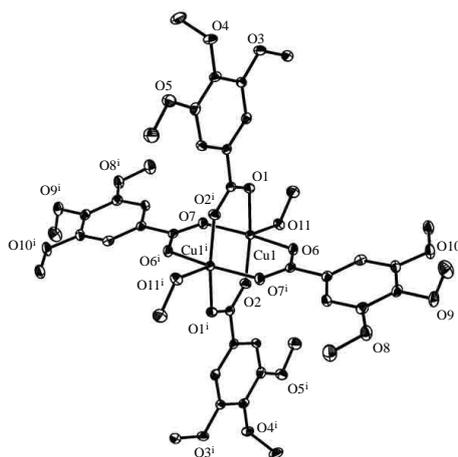
The structures were solved by direct methods, and refined by full-matrix least-squares method. The hydrogen atom attached to the coordinating methanol molecule was located from a difference Fourier map and the others were inserted at their calculated positions and fixed there. All of the calculations were carried out on a Windows 7 Core i5 computer utilizing the SHELXTL software package (Sheldrick 2008) and SHELXL-2014/7 (Sheldrick 2015). Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposit number CCDC-1570806. 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](mailto:deposit@ccdc.cam.ac.uk)).

## RESULTS AND DISCUSSION

Elemental analysis of the isolated compound showed the formulation  $[\text{Cu}_2(345\text{tmbz})_4(\text{CH}_3\text{OH})_2] \cdot 2\text{DMF}$ . IR data showed two COO stretching bands at 1574 and 1415  $\text{cm}^{-1}$  with the difference in energy characteristic of bridging carboxylate [Nakamoto, 2009]. The diffuse reflectance spectrum of  $[\text{Cu}_2(345\text{tmbz})_4(\text{CH}_3\text{OH})_2] \cdot 2\text{DMF}$  shows a strong band at 280 nm, a shoulder at 370 nm, and a broad band at 716 nm with a shoulder at lower energy side in the visible region. The former two bands can be assigned to LMCT bands from the carboxylato-oxygen to the  $\text{Cu}^{\text{II}}$  d orbital. The visible region band can be associated with d-d transitions, confirming a square-pyramidal coordination environment of the copper(II) atoms.



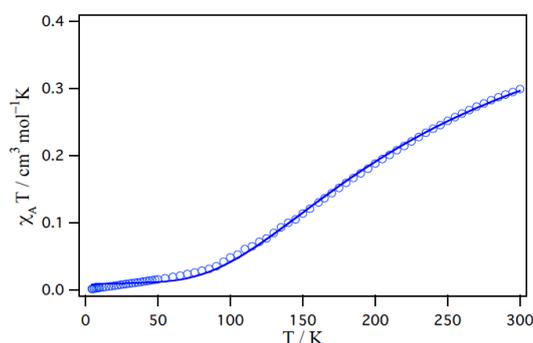
**Figure 2:** Molecular structure of  $[\text{Cu}_2(345\text{tmbz})_4(\text{CH}_3\text{OH})_2] \cdot 2\text{DMF}$ . The thermal ellipsoids are shown at the 50% probability level. Hydrogen atoms are omitted for clarity. Symmetry code: (i)  $1-x, 1-y, -z$ .



**Figure 3:** Packing diagram of  $[\text{Cu}_2(345\text{tmbz})_4(\text{CH}_3\text{OH})_2] \cdot 2\text{DMF}$ .

The molecular structure for  $[\text{Cu}_2(345\text{tmbz})_4(\text{CH}_3\text{OH})_2] \cdot 2\text{DMF}$  was drawn as an ORTEP diagram (Figure 2). The asymmetric unit contains one crystal DMF molecule and one-half of dinuclear  $[\text{Cu}_2(345\text{tmbz})_4(\text{CH}_3\text{OH})_2]$  unit with a crystallographic inversion center at the midpoint of the

Cu1 and Cu1<sup>i</sup> atoms. The dinuclear unit has a lantern-like dinuclear core bridged by four 345tmbz<sup>-</sup> ligands in a *syn-syn* fashion [Mikuriya, 2008]. The Cu1...Cu1<sup>i</sup> distance is 2.6190(6) Å, which is in the range found in dinuclear copper(II) carboxylates [Mikuriya, 2008; Mikuriya *et al.*, 1995; Mikuriya *et al.*, 2015a; Mikuriya *et al.*, 2015b; Nukada *et al.*, 1999]. The coordination geometry around each copper atom is an elongated square-pyramid. The bond distances of the Cu1 and basal O atoms are 1.9529(14)–1.9688(15) Å, which are within the normal range found in copper(II) carboxylates. The fifth position of the Cu1 atom is occupied by a methanol molecule with the Cu1-O11 distance of 2.1582(15) Å, which is also in the normal range as axial bonding for the copper(II) carboxylates [Mikuriya, 2008]. In the crystal, DMF molecules are trapped into the cavities between the dinuclear units (Figure 3).

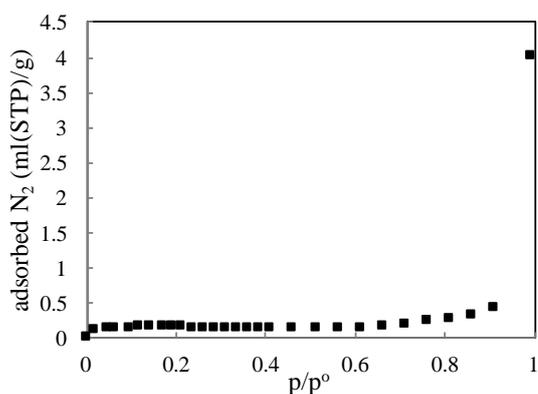


**Figure 4:** Temperature dependence of  $\chi_A T$  of  $[\text{Cu}_2(345\text{tmbz})_4(\text{CH}_3\text{OH})_2]\cdot 2\text{DMF}$ . The solid lines represent the best fit of the data.

The magnetic data of  $[\text{Cu}_2(345\text{tmbz})_4(\text{CH}_3\text{OH})_2]\cdot 2\text{DMF}$  are shown in the form of  $\chi_A T$  vs  $T$  plot (Figure 4). The magnetic moment at 300 K is  $1.55 \mu_B$  (per  $\text{Cu}^{\text{II}}$  unit), which is significantly lower than the spin-only value ( $1.73 \mu_B$ ) of  $\text{Cu}^{\text{II}}$  ( $S = 1/2$ ) ion. The magnetic moment decreases with lowering of the temperature, showing a considerable antiferromagnetic interaction between the copper(II) ions. The magnetic data were analyzed with the Bleaney-Bowers equation based on the Heisenberg model ( $H = -2JS_1 \cdot S_2$  ( $S_1 = S_2 = 1/2$ )):

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

where  $J$  is an exchange coupling constant for the two copper(II) ions,  $p$  is the fraction of mononuclear impurity, and  $Na$  is the temperature-independent paramagnetism, which was set to  $60 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$  for each copper(II) ion (Horikoshi and Mikuriya, 2005). The best-fitting parameters ( $2J = -292(2) \text{ cm}^{-1}$ ,  $g = 2.28(1)$ ,  $p = 0.0171(1)$ ) are normal as copper(II) carboxylates, showing a strong antiferromagnetic interaction between the two copper(II) ions.



**Figure 5:** N<sub>2</sub> adsorption isotherm on [Cu<sub>2</sub>(345tmbz)<sub>4</sub>(CH<sub>3</sub>OH)<sub>2</sub>] $\cdot$ 2DMF.

We expected an adsorbing ability for the present complex, if the crystal DMF molecules are lost. However, the adsorption isotherm of [Cu<sub>2</sub>(345tmbz)<sub>4</sub>(CH<sub>3</sub>OH)<sub>2</sub>] $\cdot$ 2DMF showed that the isotherm belongs to Type II in the IUPAC classification ( $S_{\text{BET}} = 0.4 \text{ m}^2\text{g}^{-1}$ ), suggesting that physical adsorption only occurred because the cavities in the crystal seem to have been still occupied by DMF molecules at the measurement.

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## REFERENCES

- Cotton, F. A., Murillo, C. A., Walton, R. A., 2005, Multiple Bonds Between Metal Atoms, 3rd ed., Springer Science and Business Media, New York, 1.
- Horikoshi, R. and Mikuriya, M., 2005, One-Dimensional Coordination Polymers from the Self-Assembly of Copper(II) Carboxylates and 4,4'-Dithiobis(pyridine), *Bull. Chem. Soc. Jpn.*, 78, 827.
- Matsushima, H., Koikawa, M., Nukada, R., Mikuriya, M., Tokii, T., 1999, Structural Characterization and Magnetic Properties of Triply Carboxylato-Bridged Dinuclear Copper(II) Complexes, *Bull. Chem. Soc. Jpn.*, 72, 1025.
- Mikuriya, M., Nukada, R., Morishita, H., and Handa, M., 1995. Chain Compounds Formed by the Reaction of Copper(II) Carboxylate [Cu<sub>2</sub>(O<sub>2</sub>CR)<sub>4</sub>] (R = C(CH<sub>3</sub>)<sub>3</sub>, CCl<sub>3</sub>) and Bridging Ligand L (L = Pyrazine, 4,4'-Bipyridine, and 1,4-Diazabicyclo[2.2.2]octane), *Chem. Lett.*, 24, 617.
- Mikuriya, M., Kida, S., Ueda, I., Tokii, T., Muto, Y., 1977. The Crystal Structure and Magnetic Property of Di- $\mu$ -propionato-*O,O'*-bis[*N-p*-tolylsalicylideneaminatocopper(II)], *Bull. Chem. Soc. Jpn.*, 50, 2464.

- Mikuriya, M., Azuma, H., Nukada, R., and Handa, M., Synthesis, 1999. X-Ray Structures, and Magnetic Properties of  $[\text{Cu}_2(\text{piv})_4(\text{Et}_3\text{N})_2]$  and  $[\text{Cu}_6(\text{piv})_6(\text{EtO})_6]$  (Hpiv = Pivalic Acid): Role of Base for Dinuclear Adduct and Oligonuclear Formation, *Chem. Lett.*, 57.
- Mikuriya, M., Azuma, H., Nukada, R., Sayama, Y., Tanaka, K., Lim, J.-W., and Handa, M., 2000a. Antiferromagnetic Adducts of Copper(II) Propionate with Pyridyl Nitronyl Nitroxides, *Bull. Chem. Soc. Jpn.*, 73, 2493.
- Mikuriya, M., Azuma, H., Handa, M., 2000b. Coordination Polymers of Copper(II) and Copper(I) Trifluoroacetates with Pyrazine, *Mol. Cryst. Liq. Cryst.*, 342, 205.
- Mikuriya, M., Azuma, H., Sun, J., Yoshioka, D., and Handa, M., 2002a. Dinuclear Copper(II) Complexes of Free Radical Carboxylic Acids, *Chem. Lett.*, 608.
- Mikuriya, M., Azuma, H., Handa, M., 2002b. Coordination Polymers of Copper(II) Propionate with Linking Ligands, *Mol. Cryst. Liq. Cryst.*, 379, 205.
- Mikuriya, M., 2008. Copper(II) Acetate as a Motif for Metal-Assembled Complexes, *Bull. Jpn. Soc. Coord. Chem.* 52, 17.
- Mikuriya, M., Yano, M., Takahashi, N., Yoshioka, D., Tanaka, H., and Handa, M., 2015a. Synthesis and Crystal Structure of a Chain Complex of Copper(II) Pivalate and 1,2-Bis(4-pyridyl)ethane in Relation to Adsorption Property for  $\text{N}_2$ , *X-ray Struct. Anal. Online*, 31, 47.
- Mikuriya, M., Yano, M., Takahashi, N., Yoshioka, D., Tanaka, H., and Handa, M., 2015b. Synthesis, crystal structure, magnetic property, and  $\text{N}_2$ -gas-adsorption property of chain compounds of dinuclear copper(II) pivalate with  $N,N'$ -bidentate ligands, *The Proceedings of the 2nd International Porous and Powder Materials Symposium and Exhibition PPM 2015*, Üç Adım Printing House, Izmir, Turkey, 72.
- Mori, W., Hoshino, H., Nishimoto, Y., and Takamizawa, S., 1999. Synthesis and Gas Occlusion of New Micropore Substance Rhodium(II) Carboxylates Bridged by Pyrazine, *Chem. Lett.*, 331.
- Nakamoto, K., 2009. *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B* (6th ed.) John Wiley & Sons, Inc, Hoboken.
- Nakashima, M., Mikuriya, M., and Muto, Y., 1985, Structural, Magnetic and IR Spectroscopic Characterization of Dinuclear Copper(II) Trichloroacetic Adduct with Benzonitrile. Nature of the Copper(II)-Benzonitrile Bond, *Bull. Chem. Soc. Jpn.*, 58, 968.
- Nukada, R., Mori, W., Takamizawa, S., Mikuriya, M., Handa, M., and Naono, H., 1999. Microporous Structure of a Chain Compound of Copper(II) Benzoate Bridged by Pyrazine, *Chem. Lett.*, 367.

Nukada, R., Mikuriya, M., Yamashita, A., and Handa, M., 2001. Mononuclear and Polynuclear Chain Compounds of Copper(II) Pivalate with *N,N'*-Didentate Ligands, Challenges for Coordination Chemistry in the New Century, Slovak Technical University Press, Bratislava, Slovakia, 83.

Nukada, R., Mikuriya, M., Handa, M., and Naono, H., 2015. Hydrophobic micropore in a chain compound of dinuclear copper(II) benzoate with pyrazine—Adsorption properties for N<sub>2</sub>, CCl<sub>4</sub>, H<sub>2</sub>O, CO<sub>2</sub>, and CH<sub>3</sub>CN. The Proceedings of the 2nd International Porous and Powder Materials Symposium and Exhibition PPM 2015, Üç Adım Printing House, Izmir, Turkey, 77.

Sheldrick, G. M., 2008. A short history of SHELX. Acta Crystallogr. Sect A, 64, 112.

Sheldrick, G. M., 2015, Crystal Structure refinement with SHELXL, Acta Crystallogr. Sect C, 71, 3.