Crystal Structure of Tetrakis(μ -2,3,6-trimethoxybenzoato- $\kappa O:\kappa O'$)bis[(methanol)-copper(II)]: Largely Rotated Benzoate Ring to the Carboxylato Bridge

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A dinuclear copper(II) carboxylate with 2,3,6-trimethoxybenzoic acid (H236-tmbz), tetrakis(μ -2,3,6-trimethoxybenzoato- $\kappa O:\kappa O'$)bis[(methanol)copper(II)], $[\text{Cu}_2(236\text{-tmbz})_4(\text{CH}_3\text{OH})_2]$, was prepared, and the crystal structure was determined by a single-crystal X-ray structure analysis at 90 K. It crystallizes in the triclinic space group $P\bar{1}$ with $a = 7.4282(11)\text{\AA}$, $b = 12.2389(18)\text{\AA}$, $c = 13.3158(19)\text{\AA}$, $\alpha = 115.128(2)^\circ$, $\beta = 95.396(3)^\circ$, $\gamma = 91.086(2)^\circ$, $V = 1088.8(3)\text{\AA}^3$, $D_x = 1.580\text{ g/cm}^3$, and $Z = 1$. The $R1$ [$I > 2\sigma(I)$] and $wR2$ (all data) values are 0.0513 and 0.1207, respectively, for all 4894 independent reflections. The two copper atoms are bridged by four 2,3,6-trimethoxybenzoato ligands in a *syn-syn* mode to form a dinuclear cluster ($\text{Cu}\cdots\text{Cu}$ 2.6071(8) $\text{\AA}$) with the apical methanol molecules. The benzoate phenyl rings are largely rotated to the bridging OCO moieties with a rotation angle (ϕ_{rot}) of 74.9(2) and 44.6(3) $^\circ$.

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Dinuclear copper(II) carboxylates have received much attention by many inorganic chemists in a related development with functional materials because of the unique paddle-wheel clusters.¹⁻¹² We recently reported on dinuclear copper(II) benzoate analogues, which have a *syn-syn*-bridged dinuclear cluster with four benzoate rings attached to three methoxy or benzyloxy groups.⁹⁻¹² Interestingly, one of these compounds exhibited a high adsorption property for N_2 , like in the case of a 1D coordination polymer of an alternated chain of dinuclear copper(II) benzoate and pyrazine.^{5,6,11} We also found that a μ -aqua-bridged 1D coordination polymer, $[\text{Cu}(246\text{-tmbz})_2(\mu\text{-H}_2\text{O})(\text{H}_2\text{O})_2]_n$, formed instead of a dinuclear cluster in the case of 2,4,6-trimethoxybenzoate (246-tmbz⁻) due to a steric hindrance of the 2,6-positioned methoxy groups.¹¹ In this paper, we focused on the molecular structure of copper(II) carboxylate with 2,3,6-trimethoxybenzoate (236-tmbz⁻) to see whether the 236-tmbz⁻ ligand constitutes a similar dinuclear cluster or not, and determined the crystal structure of the isolated complex, which has the molecular structure shown in Fig. 1.

A copper(II) carboxylate with 2,3,6-trimethoxybenzoic acid (**1**) was prepared by a similar method to those described in the literature.⁹⁻¹² A 0.5237 g (2.468 mmol) amount of 2,3,6-trimethoxybenzoic acid was added to a 5 cm^3 of 0.10 M sodium hydroxide solution. The solution was neutralized by the addition of nitric acid with a phenolphthalein indicator. To this solution, a 5 cm^3 of aqueous solution of copper(II) nitrate trihydrate (0.2992 g, 1.238 mmol) was added with stirring to give a pale-green precipitate. The precipitate was filtered off. Yield, 0.4435 g (71.1%). IR (KBr, cm^{-1}): 3410br(ν_{OH}), 3262(ν_{OH}), 2986(ν_{CH} , ring), 2944(ν_{asCH_3}), 2827(ν_{sCH_3}), 1576(ν_{asCOO}),

1491(δ_{asCH_3}), 1459(ν_{sCOO}), 1385(δ_{sCH_3}). Diffuse reflectance spectra: λ_{max} 236, 293, 382sh, 715br nm.

X-ray quality crystals were grown by recrystallization from methanol. X-ray diffraction data for the crystal were collected at 90 K on a Bruker CCD X-ray diffractometer (SMART APEX) using graphite-monochromated Mo- $K\alpha$ radiation. Crystal data and details concerning data collection are given in Table 1. The structure was solved by an intrinsic phasing method with SHELXT-2014, and refined by full-matrix least-squares methods with SHELXL-2014. Hydrogen atoms were inserted at their calculated positions, and fixed there, except for the hydrogen atom attached to the methanol oxygen atom, which was located from the D-Fourier map and refined isotropically. Crystallographic

Fig. 1 Chemical structure of the title compound.

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Table 1 Crystal and experimental data

Chemical formula: $C_{42}H_{52}Cu_2O_{22}$	
Formula weight = 1035.91	
$T = 90\text{ K}$	
Crystal system: triclinic	Space group: $P\bar{1}$
$a = 7.4282(11)\text{ \AA}$	$\alpha = 115.128(2)^\circ$
$b = 12.2389(18)\text{ \AA}$	$\beta = 95.396(3)^\circ$
$c = 13.3158(19)\text{ \AA}$	$\gamma = 91.086(2)^\circ$
$V = 1088.8(3)\text{ \AA}^3$	$Z = 1$
$D_x = 1.580\text{ g/cm}^3$	
Radiation: Mo $K\alpha$ ($\lambda = 0.71073\text{ \AA}$)	
$\mu(\text{Mo } K\alpha) = 1.064\text{ mm}^{-1}$ $F(0\ 0\ 0) = 538$	
Crystal size = $0.18 \times 0.12 \times 0.08\text{ mm}^3$	
No. of reflections collected = 6959	
No. of independent reflections = 4894	
θ range for data collection: 1.700 to 27.498°	
Data/Restraints/Parameters = 4894/0/309	
Goodness-of-fit on $R^2 = 0.993$	
R indices [$I > 2\sigma(I)$]: $R1 = 0.0513$, $wR2 = 0.1084$	
R indices (all data): $R1 = 0.0762$, $wR2 = 0.1207$	
$(\Delta/\sigma)_{\max} = 0.000$	
$(\Delta\rho)_{\max} = 0.652\text{ e \AA}^{-3}$ $(\Delta\rho)_{\min} = -0.621\text{ e \AA}^{-3}$	
Measurement: Bruker Smart APEX CCD diffractometer	
Program system: SHELXTL	
Structure determination: intrinsic phasing method (SHELXT-2014/5)	
Refinement: full matrix least-squares (SHELXL-2014/7)	
CCDC deposition number: 2063228

Fig. 2 ORTEP view of the title compound. Hydrogen atoms are omitted for clarity. The thermal ellipsoids are shown at the 50% probability level. Prime denotes the symmetry code: $(1-x, 1-y, 1-z)$.

data have been deposited with Cambridge Crystallographic Data Centre (Deposit numbers CCDC-2063228).

The molecular structure, drawn as an ORTEP diagram, is shown in Fig. 2. Selected bond distances and angles are given in Table 2. The molecule is a dinuclear copper(II) cluster of $[\text{Cu}_2(236\text{-tmbz})_4(\text{CH}_3\text{OH})_2]$ with four 2,3,6-trimethoxybenzoato ligands in a *syn-syn* fashion, which has a crystallographic center of symmetry. The $\text{Cu1}\cdots\text{Cu1}'$ distance is $2.6071(8)\text{ \AA}$, which is in the normal range found in dinuclear copper(II) carboxylates.¹⁻³ The coordination geometry around each copper atom is an

Table 2 Selected bond distances ($\text{\AA}$) and angles ($^\circ$)

$\text{Cu1}\cdots\text{Cu1}'$	$2.6071(8)$	$\text{Cu1}\cdots\text{O1}$	$1.951(2)$
$\text{Cu1}\cdots\text{O2}'$	$1.967(2)$	$\text{Cu1}\cdots\text{O6}$	$1.968(2)$
$\text{Cu1}\cdots\text{O7}'$	$1.974(2)$	$\text{Cu1}\cdots\text{O11}$	$2.137(2)$
$\text{O1}\cdots\text{Cu1}\cdots\text{O2}'$	$169.57(9)$	$\text{O1}\cdots\text{Cu1}\cdots\text{O6}$	$88.15(9)$
$\text{O1}\cdots\text{Cu1}\cdots\text{O7}'$	$87.71(9)$	$\text{O1}\cdots\text{Cu1}\cdots\text{O11}$	$97.41(9)$
$\text{O2}'\cdots\text{Cu1}\cdots\text{O6}$	$92.12(9)$	$\text{O2}'\cdots\text{Cu1}\cdots\text{O7}'$	$90.08(9)$
$\text{O2}'\cdots\text{Cu1}\cdots\text{O11}$	$92.95(9)$	$\text{O6}\cdots\text{Cu1}\cdots\text{O7}'$	$168.83(9)$
$\text{O6}\cdots\text{Cu1}\cdots\text{O11}$	$95.21(9)$	$\text{O7}'\cdots\text{Cu1}\cdots\text{O11}$	$95.61(9)$

Prime denotes the symmetry code: $(1-x, 1-y, 1-z)$.

Fig. 3 Definition of the bending (ϕ_{bend}) and rotating (ϕ_{rot}) angles of the benzoate group.

elongated square-pyramid. The bond lengths of the Cu1 and basal O atoms are $1.951(2)$ – $1.974(2)\text{ \AA}$ and the apical $\text{Cu1}\cdots\text{O11}$ distance is $2.137(2)\text{ \AA}$, which are also in the normal range as the $\text{Cu}\cdots\text{O}(\text{basal})$ and $\text{Cu}\cdots\text{O}(\text{apical})$ distances for the copper(II) carboxylates.¹⁻³ The Cu1 atom is $0.180(1)\text{ \AA}$ above the basal plane, defined by the four 2,3,6-trimethoxybenzoato-oxygen atoms toward the apical methanol-oxygen atom. The benzoate bridging moieties are not coplanar, as found in the related dinuclear copper(II) benzoates.^{1,9-12} The dihedral angle between the $\text{O1}\cdots\text{C7}\cdots\text{O2}$ (or $\text{O6}\cdots\text{C17}\cdots\text{O7}$) and $\text{Cu1}\cdots\text{O1}\cdots\text{O2}\cdots\text{Cu1}'$ (or $\text{Cu1}\cdots\text{O6}\cdots\text{O7}\cdots\text{Cu1}'$) planes, which denotes the bending angle (ϕ_{bend})¹ of the carboxylato OCO plane in the carboxylato-bridge, is $7.1(5)^\circ$ (or $7.0(3)^\circ$). On the other hand, the dihedral angle between the $\text{O1}\cdots\text{C7}\cdots\text{O2}$ (or $\text{O6}\cdots\text{C17}\cdots\text{O7}$) and $\text{C1}\cdots\text{C2}\cdots\text{C3}\cdots\text{C4}\cdots\text{C5}\cdots\text{C6}$ (or $\text{C11}\cdots\text{C12}\cdots\text{C13}\cdots\text{C14}\cdots\text{C15}\cdots\text{C16}$) planes, which denotes the rotation angle (ϕ_{rot})¹ of the benzoate ring relative to the OCO plane, as depicted in Fig. 3, is $74.9(2)^\circ$ (or $44.6(3)^\circ$). In the present complex, the rotation angles, ϕ_{rot} , are much larger among the dinuclear copper(II) benzoate analogues, except for the μ -aqua-bridged 1D polynuclear complex $[\text{Cu}(246\text{-tmbz})_2(\mu\text{-H}_2\text{O})(\text{H}_2\text{O})_2]_n$, although the bending angles, ϕ_{bend} , are comparable to those of the related copper(II) benzoate derivatives,⁹⁻¹² listed in Table 3, and those of other copper(II) benzoates [$\phi_{\text{bend}} = 1.5(4) - 11.4(3)^\circ$ and $\phi_{\text{rot}} = 5.3(4) - 19.5(8)^\circ$].¹ The large rotation of the benzoate rings was observed for only the cases involving the dinuclear complex $[\text{Cu}_2(236\text{-tmbz})_4(\text{CH}_3\text{OH})_2]$ and the 1D polynuclear complex $[\text{Cu}(246\text{-tmbz})_2(\mu\text{-H}_2\text{O})(\text{H}_2\text{O})_2]_n$,¹¹ suggesting that the presence of the 2- and 6-methoxy groups of the benzoate ring may induce a large deviation from coplanarity with the adjacent carboxy group, possibly because of an electrostatic repulsion between the methoxy-oxygen and the carboxy-oxygen atoms. As shown in Fig. 4, the dinuclear clusters are loosely connected to each other by hydrogen bondings between the apical methanol molecules and the carboxylato-oxygen atoms of the neighboring dinuclear molecules [$\text{O11}\cdots\text{O7}(x-1, y, z)$ $2.740(3)\text{ \AA}$], resulting in no voids in the crystal.

Table 3 Structural comparison of the copper(II) benzoates

Complex	Cu–Cu (Å)	Cu–O(basal) (Å)	Cu–O(apical) (Å)	ϕ_{bend} (°)	ϕ_{rot} (°)
[Cu ₂ (345-tmbz) ₄ (CH ₃ OH) ₂] ⁹	2.6190(6)	1.953(1) – 1.969(2)	2.158(2)	2.8(2), 2.9(3)	7.6(2), 8.5(3)
[Cu ₂ (345-tbng) ₄ (dmf) ₂] ¹⁰	2.6345(12)	1.957(3) – 1.977(3)	2.166(3)	5.9(2), 9.4(1)	4.5(3), 11.0(3)
[Cu ₂ (245-tmbz) ₄ (CH ₃ OH) ₂] ¹²	2.5847(5)	1.962(1) – 1.969(1)	2.133(1)	1.3(3), 3.1(3)	10.4(3), 21.6(2)
[Cu ₂ (234-tmbz) ₄ (CH ₃ OH) ₂] ¹¹	2.6009(7)	1.950(2) – 1.983(2)	2.131(2)	1.9(3), 5.9(4)	30.3(3), 38.3(2)
[Cu ₂ (236-tmbz) ₄ (CH ₃ OH) ₂] ^a	2.6071(8)	1.951(2) – 1.974(2)	2.137(2)	7.0(3), 7.1(5)	44.6(3), 74.9(2)
[Cu(246-tmbz) ₂ (μ -H ₂ O)(H ₂ O) ₂] _n ¹¹	4.1420(5)	1.946(2) – 2.058(2)	2.302(1)	14.4(4) ^b	64.0(2)

a. This work. b. The dihedral angle between the O–C–O and Cu–O–O–O planes.

Fig. 4 Packing diagram of the title compound. The dotted lines denote the hydrogen bonds between the apical methanols and the 2,3,6-trimethoxybenzoato-oxygen atoms of the neighboring dinuclear clusters.

In this study, we found that the dinuclear cluster can be formed in the case of 2,3,6-trimethoxybenzoate, meaning that more flexibility occurs to compromise with the steric hindrance of the neighboring 2,3,6-trimethoxy groups attached to the adjacent benzoate rings to form the paddle-wheel cluster, compared with the case for 2,4,6-trimethoxybenzoate, which may be difficult to compromise with the steric hindrance because of the symmetrical substituent positions of the three methoxy groups.

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References

1. T. Kawata, H. Uekusa, S. Ohba, T. Furukawa, T. Tokii, and Y. Muto, *Acta Crystallogr., Sect. B*, **1992**, *48*, 253.
2. M. R. Sundberg, R. Uggla, and M. Melnik, *Polyhedron*, **1996**, *15*, 1157.
3. M. Mikuriya, *Bull. Jpn. Soc. Coord. Chem.*, **2008**, *52*, 17.
4. R. Scatena, Y. T. Guntern, and P. Macci, *J. Am. Chem. Soc.*, **2019**, *141*, 9382.
5. R. Nukada, W. Mori, S. Takamizawa, M. Mikuriya, M. Handa, and H. Naono, *Chem. Lett.*, **1999**, *28*, 367.
6. R. Nukada, M. Mikuriya, M. Handa, and H. Naono, in “*The Proceedings of the 2nd International Porous and Powder Materials Symposium and Exhibition PPM 2015*”, ed. S. K. Ozdemir, M. Polat, and M. Tanoglu, **2015**, Uc Adim Printing House, Izmir, 77 – 81.
7. M. Mikuriya, M. Yano, N. Takahashi, D. Yoshioka, H. Tanaka, and M. Handa, *X-ray Struct. Anal. Online*, **2015**, *31*, 47.
8. M. Mikuriya, R. Indrawati, R. Hashido, S. Matsubara, C. Nakamura, D. Yoshioka, K. Yokota, M. Fukuzaki, and M. Handa, *Magnetochemistry*, **2018**, *4*, 22.
9. M. Mikuriya, C. Yamakawa, K. Tanabe, D. Yoshioka, R. Mitsuhashi, H. Tanaka, and M. Handa, *J. Turkish Chem. Soc., Sect. A*, **2018**, *5(sp.is.1)*, 103.
10. M. Mikuriya, C. Yamakawa, N. Masuda, D. Yoshioka, S. Yamaguchi, H. Yamada, T. Mizuta, N. Kawata, H. Tanaka, and M. Handa, *Open Chem. J.*, **2019**, *6*, 19.
11. M. Mikuriya, C. Yamakawa, K. Tanabe, R. Nukita, Y. Amabe, D. Yoshioka, R. Mitsuhashi, R. Tatehata, H. Tanaka, M. Handa, and M. Tsuboi, *Magnetochemistry*, **2021**, *7*, 35.
12. M. Mikuriya, C. Yamakawa, K. Tanabe, R. Nukita, D. Yoshioka, R. Mitsuhashi, H. Tanaka, M. Handa, and M. Tsuboi, *X-ray Struct. Anal. Online*, **2021**, *37*, 35.