

Article

Copper(II) Carboxylates with 2,3,4-Trimethoxybenzoate and 2,4,6-Trimethoxybenzoate: Dinuclear Cu(II) Cluster and μ -Aqua-Bridged Cu(II) Chain Molecule

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Abstract: Copper(II) complexes with 2,3,4-trimethoxybenzoic acid (H234-tmbz) and 2,4,6-trimethoxybenzoic acid (H246-tmbz), [Cu₂(234-tmbz)₄(H₂O)₂] (**6**) and [Cu(246-tmbz)₂(μ -H₂O)₂(H₂O)₂]_n (**7**), were synthesized and characterized by elemental analysis, infrared and UV-vis spectra and temperature dependence of magnetic susceptibilities (1.9–300 K). The X-ray crystal structures revealed that the former **6** is a dinuclear cluster having *syn-syn*-bridged Cu₂(μ -234-tmbz)₄ core with Cu...Cu separation of 2.6009(7) Å, while the latter **7** is a μ -aqua-bridged chain molecule consisting of Cu(246-tmbz)₂(μ -H₂O)₂(H₂O)₂ units with Cu...Cu separation of 4.1420(5) Å. Temperature dependence of magnetic susceptibilities showed that an antiferromagnetic interaction with $2J = -272$ cm⁻¹ for **6** and a weak antiferromagnetic interaction with $J = -0.21$ cm⁻¹ for **7**, between the two copper(II) ions. The adsorption isotherm of **6** showed Types I behavior having a 125.4 m²g⁻¹ of specific surface area.

Keywords: copper(II) carboxylate; 2,3,4-trimethoxybenzoic acid; 2,4,6-trimethoxybenzoic acid; magnetic property; antiferromagnetic interaction; adsorption property

1. Introduction

Copper acetate is known as one of the oldest compounds as dinuclear metal clusters and became popular since the discovery of the paddle-wheel or lantern-type dinuclear core with four *syn-syn* bridging acetate ligands for the two copper(II) ions, which interact with each other by an antiferromagnetic spin-coupling [1,2]. A great number of dinuclear copper(II) carboxylates have been prepared and their magnetic properties and crystal structures have been studied in order to elucidate the magneto structural correlations [3–11]. In most cases, dinuclear clusters with the paddle-wheel or lantern-type core have been found to have a general formula [Cu₂(RCOO)₄L₂] (L = H₂O, CH₃OH, DMF, CH₃CN, etc.), forming discrete dinuclear carboxylates and their adducts. In other cases, 1-D coordination polymers can be formed with linking ligands, which connect the axial sites of the dinuclear clusters. We have engaged in the synthesis of such copper acetate analogues and their coordination polymers [11–18]. Previously, we found that a chain compound of copper(II) benzoate with pyrazine [Cu₂(bz)₄(pyz)]_n (**1**) (Hbz = benzoic acid, pyz = pyrazine) (Figure 1) forms a hydrophobic micropore surrounded by the aromatic benzoate groups in the crystal and has a high adsorption ability for N₂, recognizing from other gas molecules such as

H₂O and CCl₄ [12,13]. In order to extend copper(II) benzoate analogues, we introduced three substituent groups into the benzoate ring. We could isolate an analogous dinuclear cluster [Cu₂(345-tmbz)₄(CH₃OH)₂] (2) by the use of 3,4,5-trimethoxybenzoic acid (H345-tmbz) as a carboxylate ligand [16]. The X-ray structure analysis revealed a lantern-type core with Cu-Cu distance of 2.6190(6) Å [16]. We also found a similar dinuclear cluster [Cu₂(tbnz)₄(DMF)₂] (DMF = *N,N*-dimethylformamide) (3) by the use of much more bulky benzyl group-containing benzoic acid, 3,4,5-tri-*O*-benzylgalic acid (Htbnz) [18]. Unfortunately, these compounds did not show a good adsorption property for N₂, irrespective of the introduction of bulky groups. In case of ruthenium, we isolated a dinuclear cluster with deuterated 3,4,5-tri(ethoxy-*d*₅)benzoic acid (H345-tedbz) [Ru₂(345-tedbz)₄(H₂O)₂]⁺ (4), which enabled us to interpret the ¹HNMR spectra of the chlorido-bridged chain complex [Ru₂(345-tedbz)₄Cl]_{*n*}, suggesting the rotation of the benzoate phenyl ring in solution [19,20]. We also prepared many chlorido-bridged chain compounds [Ru₂(345-tRbz)₄Cl]_{*n*} (5) by the use of a series of 3,4,5-trialkoxybenzoic acid (H345-tRbz) [21,22], as shown in Figure 1. In these dinuclear ruthenium carboxylates, liquid-crystalline properties [21] and magnetic faster effect [22] were found by introducing long alkyl chain groups at the 3, 4, 5-positions of the benzoate rings, exploring a new aspect of these compounds. In this study, we selected 2,3,4-trimethoxybenzoic acid (H234-tmbz) and 2,4,6-trimethoxybenzoic acid (H246-tmbz) as carboxylic acids in order to put three methoxy groups at the 2, 3, 4- and 2, 4, 6- positions of the benzoate rings in the hope of finding the substitution-position effect to construct new copper(II) carboxylates (Figure 2). This paper reports the synthesis, spectroscopic and magnetic properties, and crystal structures of the isolated compounds, the copper(II) carboxylate with 234-tmbz[−] (6) and the copper(II) carboxylate with 246tmbz[−] (7). The adsorption property of 6 for N₂ is also reported.

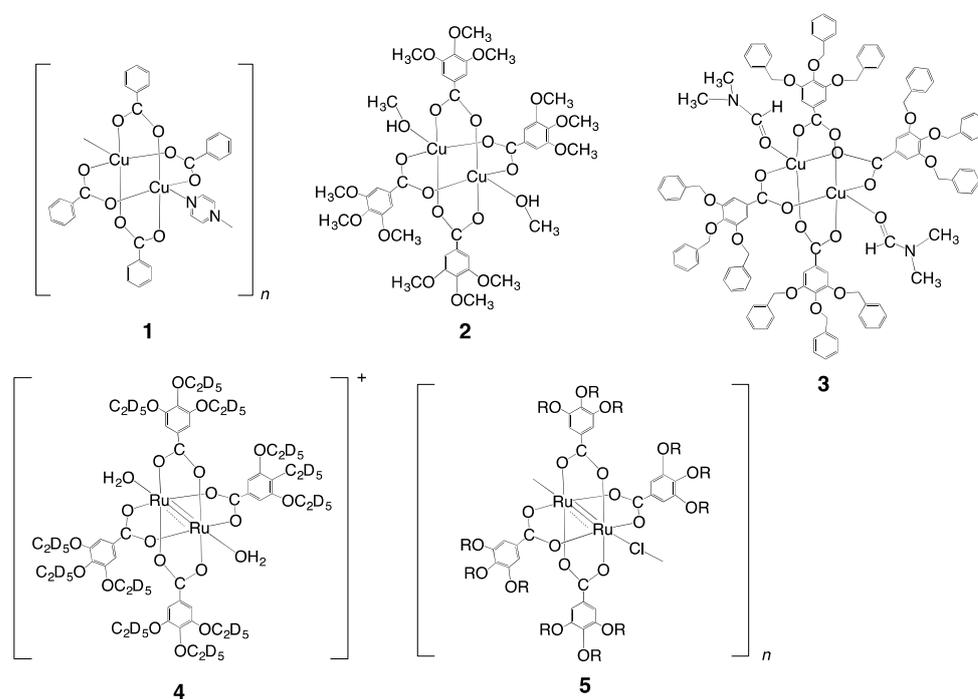


Figure 1. Lantern-type dinuclear metal carboxylates and chain compounds of metal carboxylates with linking ligands: [Cu₂(bz)₄(pyz)]_{*n*} (1), [Cu₂(345-tmbz)₄(CH₃OH)₂] (2), [Cu₂(tbnz)₄(DMF)₂] (3), [Ru₂(345-tedbz)₄(H₂O)₂]⁺ (4), and [Ru₂(345-tRbz)₄Cl]_{*n*} (5).

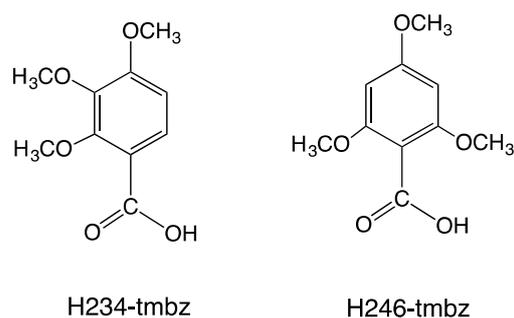


Figure 2. 2,3,4-Trimethoxybenzoic acid (H234-tmbz) and 2,4,6-trimethoxybenzoic acid (H246-tmbz).

2. Results and Discussion

2.1. Synthesis of Copper(II) Carboxylates

The present copper(II) carboxylates were synthesized according to a similar method to that described for the dinuclear cluster $[\text{Cu}_2(345\text{-tmbz})_4(\text{CH}_3\text{OH})_2]$ (**2**) [16]. Reaction of 2,3,4-trimethoxybenzoic acid and copper(II) nitrate in the neutral aqueous solution afforded pale blue precipitate (**6**), while the reaction of 2,4,6-trimethoxybenzoic acid with copper(II) nitrate gave greenish precipitate (**7**). Elemental analysis data of the isolated compounds are in accordance with the formulation of the dinuclear $[\text{Cu}_2(234\text{-tmbz})_4(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ for **6** and the mononuclear $[\text{Cu}(246\text{-tmbz})_2(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$ or dinuclear $[\text{Cu}_2(246\text{-tmbz})_4(\text{H}_2\text{O})_2] \cdot 8\text{H}_2\text{O}$ or polynuclear $[\text{Cu}(246\text{-tmbz})_2(\mu\text{-H}_2\text{O})_2(\text{H}_2\text{O})_2]_n \cdot n\text{H}_2\text{O}$ for **7**, respectively.

2.2. Infrared Spectra of Copper(II) Carboxylates

In the infrared spectra of the complex **6**, antisymmetric and symmetric stretching bands for COO^- group were observed at 1602 and 1468 cm^{-1} with the energy difference of $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ of 134 cm^{-1} , which is similar to those observed for dinuclear copper(II) carboxylates with *syn-syn* mode of carboxylato bridges [15,23]. On the other hand, the complex **7** exhibited two COO stretching bands at 1608 and 1414 cm^{-1} with the greater separation of $\Delta\nu$ of 194 cm^{-1} , which is characteristic of monodentate coordination of carboxylate ligands [15,23], and consistent with the crystal structure, as described in Section 2.4. The strong band at 3441 cm^{-1} in **6** can be assigned to OH stretching band of coordinated or crystallization water molecules [23]. The four medium bands at around 3634–3120 cm^{-1} in **7** also can be assigned as OH stretching bands, suggesting the presence of bridging water molecules as well as coordinated and crystal water molecules in the compound [24,25]. It is known that the frequency shift of the $\nu(\text{OH})$ bands to the lower energy side is indicative of the hydrogen bonded state of the water molecules [26]. The stretching vibrations of the CH_3 of methoxy groups appeared at 2941 and 2839 cm^{-1} in **6** and 2948 and 2840 cm^{-1} in **7**, respectively, confirming the presence of the methoxy groups of 2,3,4-trimethoxybenzoate and 2,4,6-trimethoxybenzoate ligands, respectively [26].

2.3. Electronic Spectra of Copper(II) Carboxylates

The diffused reflectance spectra of the present complexes are shown in Figure 3. The spectra of **6** show a broad band at around 246 and 286 nm, which can be assigned to ligand-to-metal charge transfer bands in the UV-region, a shoulder band at around 360 nm, which can be a distinctive CT band characteristic of copper acetate type dinuclear clusters [3,7,11], and a broad band assignable to d-d transitions at around 706 nm. The d-d band of **6** is located at higher energy side compared with that of **7**. Moreover, the typical broad asymmetric band with a shoulder at around 1000 nm is in harmony with the distorted square pyramidal coordination of copper(II) [27] as found in the crystal structure of **6**. On the other hand, the spectra of **7** can be characterized as four absorption bands, being a little different from those previously reported for copper acetate type clusters, lacking a distinctive shoulder-like absorption at near-UV region. The absorption bands at 212, 254, and 310 nm can be assigned to ligand to metal charge transfer bands, which are responsible for the high intensity bands in the UV region. Furthermore, a broad band at 750 nm

spanned in the visible and NIR regions until around 1200 nm is typically interpreted as d-d transitions of the elongated octahedral copper(II) [27], which is observed for the crystal structure of 7 in Section 2.4.

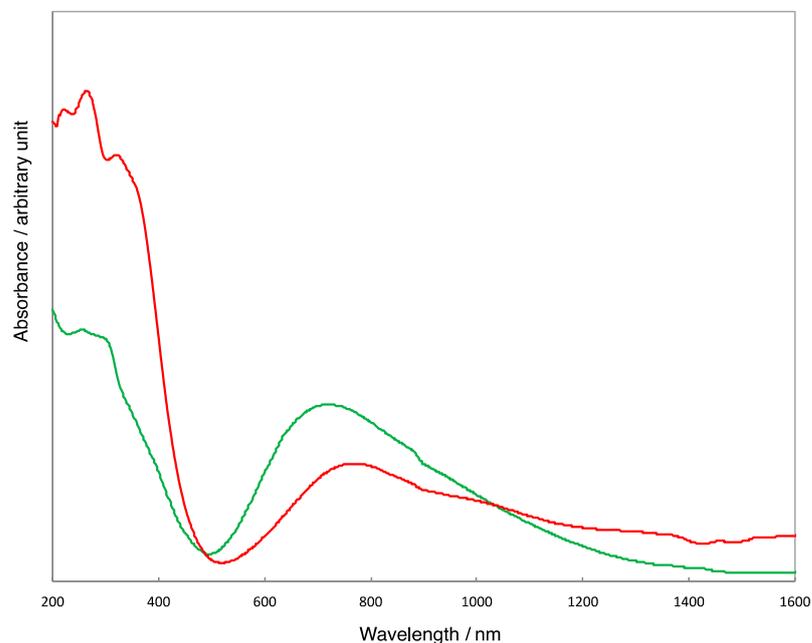


Figure 3. Diffused reflectance spectra of $[\text{Cu}_2(234\text{-tmbz})_4(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ (6) (green line) and $[\text{Cu}(246\text{-tmbz})_2(\mu\text{-H}_2\text{O})_2(\text{H}_2\text{O})_2]_n \cdot n\text{H}_2\text{O}$ (7) (red line).

2.4. Crystal Structures of Copper(II) Carboxylates

Single crystals were obtained by recrystallization from methanol for complexes 6 and 7. Crystal data and details concerning data collection are given in Table 1. Selected bond lengths and angles are listed in Table 2. Both of the presented complexes crystallized in the monoclinic lattice. As for 6, the crystal contains coordinating methanol molecules with a formula $[\text{Cu}_2(234\text{-tmbz})_4(\text{CH}_3\text{OH})_2]$ (6'), slightly different from 6. A perspective view of the molecular structure of 6' is shown in Figure 4. The asymmetric unit consists of half of a $[\text{Cu}_2(234\text{-tmbz})_4(\text{CH}_3\text{OH})_2]$ molecule with the crystallographic inversion center at the midpoint of the Cu_2 core. The molecule has a copper acetate type dinuclear core with four *syn-syn* carboxylate-bridges and the structure is similar to that of the one reported for $[\text{Cu}_2(345\text{-tmbz})_4(\text{CH}_3\text{OH})_2]$ [16]. The copper atom is coordinated by four carboxylate oxygen atoms of 234-tmbz[−] with the Cu1-O distances of 1.9504(18)–1.9827(17) Å and an apical oxygen atom of methanol with the Cu1-O11 distance of 2.1309(19) Å to form a distorted square pyramidal geometry. The apical methanol molecules came from the recrystallization solvent. The copper atom lies on the basal O_4 plane toward the apical oxygen atom by 0.178 Å. The Cu...Cu' distance is 2.6009(7) Å, which is normal as found in copper(II) acetate type dinuclear clusters [4–11]. This feature is originated from the *pseudo* Jahn–Teller distortion of copper(II) ion and has been similarly observed in copper(II) acetate type clusters. The relationship between the Cu...Cu distance and apical coordination was recently elucidated [28,29]. The coordination of apical ligand weakens the Cu-Cu interaction which becomes longer upon the apical coordination and the distortion of the Cu atom from the planar arrangement can be understood to be due to electrostatic attraction between the Cu(II) and apical ligand's dipole moment, reflecting *trans* influence of apical ligand [29]. The benzoate moieties are not planar as like the related dinuclear copper(II) benzoate analogues [8,30,31]. The dihedral angle (ϕ_{bend}) between the O1-C7-O2 plane of the carboxylato bridge and the Cu1-O1...O2-Cu1' plane and the dihedral angle (ϕ_{rot}) between the O1-C7-O2 plane and the benzoate C1-C2-C3-C4-C5-C6 ring are 1.9(3)° and 38.3(2)°, respectively. The ϕ_{bend} and ϕ_{rot} angles for the O6-C17-O7, Cu1-O6...O7-Cu1',

and C11-C12-C13-C14-C15-C16 planes are $5.9(4)^\circ$ and $30.3(3)^\circ$, respectively. The distortion from the planar arrangement may be due to the packing effect in the crystal. As shown in Figure 5, the dinuclear molecules are loosely bound to the adjacent dinuclear molecules by the hydrogen bonds between the apical methanol molecules and the carboxylate-oxygen atoms of the neighbor dinuclear molecules [O11...O2($x, 1 + y, z$) 2.819 Å]. In the crystal, the hydrogen-bonded array of the dinuclear molecules are related by the crystallographic C_2 axis to the neighboring the hydrogen-bonded array of the dinuclear molecules. A perspective view of the molecular structure of 7 is depicted in Figure 6. The asymmetric unit consists of half of a [Cu(246-tmbz)₂(μ -H₂O)₂(H₂O)₂] molecule with the crystallographic inversion center at the Cu1 atom and one crystallizing water molecule. Unexpectedly, the complex is essentially polynuclear copper(II) complex [Cu(246-tmbz)₂(μ -H₂O)₂(H₂O)₂]_n with two monodentate 246-tmbz[−] ligands and four aqua ligands in an elongated octahedral geometry. The equatorial Cu1-O1 and Cu1-O6 distances are 2.0583(18) Å and 1.9461(18) Å, respectively, and the axial Cu1-O7 distance is 2.3018(12) Å, which is typical as due to the *pseudo* Jahn–Teller distortion of copper(II) ion. The other oxygen atom (O2) of the monodentate 246-tmbz[−] is hydrogen-bonded to the axial aqua-oxygen atom (O7) [O2...O7 2.645 Å]. The equatorial aqua-oxygen atom (O6) is also hydrogen bonded to the crystallization water molecule (O8) [O6...O8 2.661 Å]. The equatorial moieties including the 246-tmbz[−] ligands of the mononuclear unit are not coplanar, with the dihedral angle between the equatorial O1-O6-O1'-O6' plane around the Cu1 atom and the benzoate ring C1-C2-C3-C4-C5-C6 plane, of $40.14(7)^\circ$. The dihedral angle (ϕ_{rot}) between the O1-C7-O2 plane and the benzoate C1-C2-C3-C4-C5-C6 ring is $64.0(2)^\circ$, disclosing the severe rotated arrangement of the benzoate ring from the carboxylate moiety, compared with that of 6'. This rotation of the benzoate ring would force a sterically crowded state between the 2,6-methoxy groups of neighboring four 246-tmbz[−] ligands, if the dinuclear [Cu₂(246-tmbz)₄] cluster was constructed, resulting in the formation of the present polynuclear chain molecule instead of the dinuclear cluster. In the crystal, the O7 atom of the aqua ligand is located at the crystallographic C_2 axis and thus, the mononuclear [Cu(246-tmbz)₂(μ -H₂O)₂(H₂O)₂] units are connected by the axial aqua molecules with the closest contact of Cu1...Cu1(1 - $x, y, 3/2 - z$) of 4.1420(5) Å and the Cu1-O7-Cu1(1 - $x, y, 3/2 - z$) angle of $128.24(12)^\circ$, to form an infinite chain molecule as shown in Figure 7.

Table 1. Crystal data for 6' and 7.

	6'	7
Empirical formula	C ₄₂ H ₅₂ Cu ₂ O ₂₂	C ₂₀ H ₃₂ CuO ₁₅
Formula weight	1035.91	575.99
Temperature/K	90	90
Crystal dimensions/mm	0.30 × 0.22 × 0.11	0.40 × 0.22 × 0.06
Crystal system	monoclinic	monoclinic
Space group	C2/c	C2/c
<i>a</i> /Å	26.014(4)	28.686(3)
<i>b</i> /Å	7.4409(12)	10.4617(11)
<i>c</i> /Å	24.510(4)	8.2841(9)
β /°	105.174(3)	101.792(2)
<i>V</i> /Å ³	4579.0(13)	2433.6(5)
<i>Z</i>	4	4
<i>d</i> _{calcd.} /gcm ^{−3}	1.503	1.572
μ /mm ^{−1}	1.012	0.973
<i>F</i> (000)	2152	1204
Reflections collected	14670	7502
Independent reflections (<i>R</i> _{int})	5524 (0.0441)	2947 (0.0385)
θ range for data collection	1.722 to 28.490°	2.902 to 28.435
Data/Restraints/Parameters	5524/0/309	2947/2/188
<i>R</i> 1, <i>wR</i> 2 [<i>I</i> > 2 σ (<i>I</i>)] ^[a]	0.0430, 0.1124	0.0458, 0.1023
<i>R</i> 1, <i>wR</i> 2 (all data) ^[a]	0.0622, 0.1282	0.0658, 0.1131
Goodness-of-fit on <i>F</i> ²	0.820	1.038
CCDC number	1570723	2060931

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

Table 2. Selected bond distances (Å) and angles (°), with esds in parentheses for **6'** and **7**. Prime in **6'** denotes the symmetry position (1 - x, 1 - y, 1 - z). Prime and double prime in **7** denotes the symmetry positions (1 - x, 2 - y, 1 - z) and (1 - x, y, 3/2 - z), respectively.

6'			
Cu1...Cu1'	2.6009(7)	Cu1-O6	1.9504(18)
Cu1-O1	1.9827(17)	Cu1-O7'	1.9574(17)
Cu1-O2'	1.9802(17)	Cu1-O11	2.1309(19)
O1-Cu1-O2'	169.71(7)	O2'-Cu1-O7'	90.54(7)
O1-Cu1-O6	90.72(7)	O2'-Cu1-O11	96.23(7)
O1-Cu1-O7'	88.75(7)	O6-Cu1-O7'	169.47(7)
O1-Cu1-O11	94.05(7)	O6-Cu1-O11	98.36(8)
O2'-Cu1-O6	88.11(8)	O7'-Cu1-O11	92.16(7)
7			
Cu1-Cu1''	4.1420(5)	Cu1-O6	1.9461(18)
Cu1-O1	2.0583(18)	Cu1-O7	2.3018(12)
O1-Cu1-O1''	180.0	O1-Cu1-O7	85.61(6)
O1-Cu1-O6	87.65(7)	O1-Cu1-O7'	180.0
O1-Cu1-O6'	92.35(8)	O7-Cu1-O7'	180.0
Cu1-O7-Cu1''	128.24(12)		

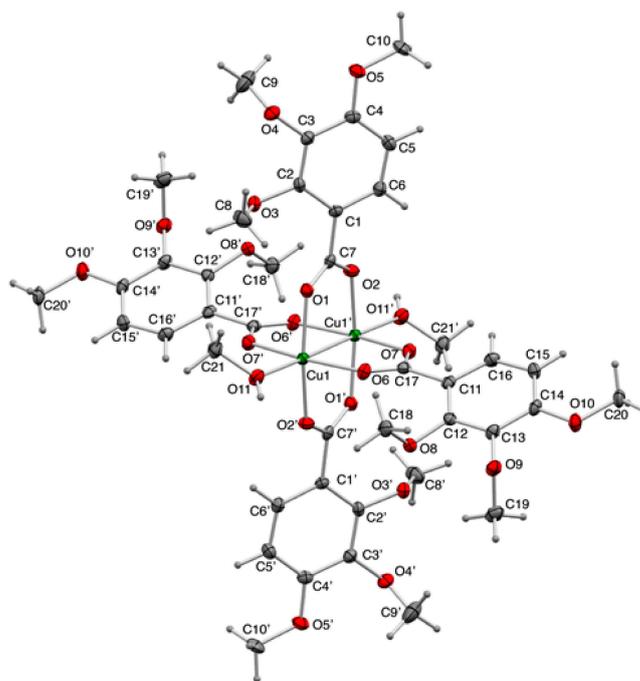


Figure 4. ORTEP view of the molecular structure for $[\text{Cu}_2(234\text{-tmbz})_4(\text{CH}_3\text{OH})_2]$ (**6'**) with 50% thermal ellipsoids. Prime denotes the symmetry position (1 - x, 1 - y, 1 - z).

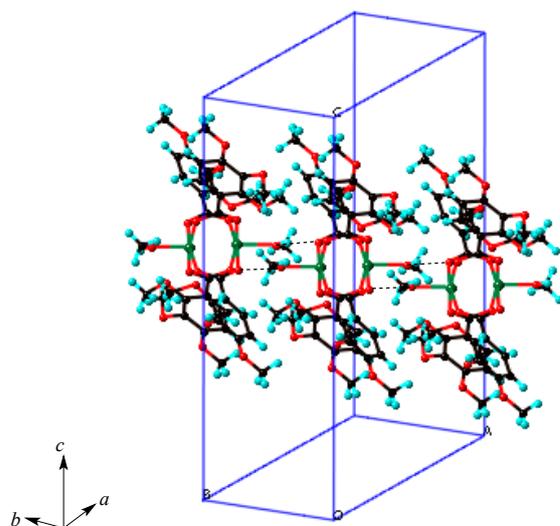


Figure 5. View of the hydrogen-bonded array of the dinuclear molecules in $6'$. Dotted lines denote the hydrogen bonds between the apical methanol molecules and the carboxylate-oxygen atoms of the neighboring dinuclear molecules.

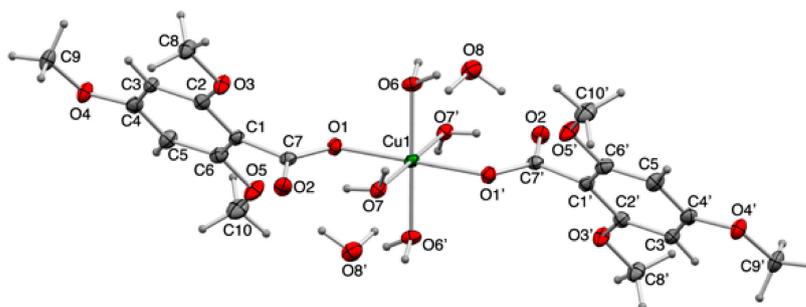


Figure 6. ORTEP view of the molecular structure for $[\text{Cu}(\text{246-tmbz})_2(\mu\text{-H}_2\text{O})_2(\text{H}_2\text{O})_2]_n \cdot 2n\text{H}_2\text{O}$ (7) with 50% thermal ellipsoids. Prime denotes the symmetry position $(1 - x, 2 - y, 1 - z)$.

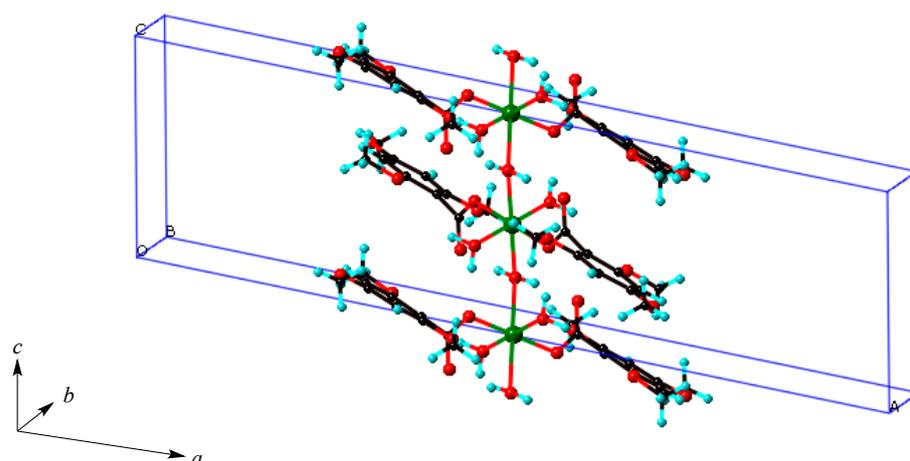


Figure 7. Fragment of the polynuclear chain molecule in 7 .

2.5. Magnetic Properties of Copper(II) Carboxylates

The magnetic data for complex 6 is displayed in Figure 8 as the temperature variation of effective magnetic moment (μ_M) and magnetic susceptibility (χ_M) per dinuclear unit. The effective magnetic moment of 6 at 300 K is $1.53 \mu_B$ per Cu atom, which is lower than the spin-only value of $1.73 \mu_B$ for a magnetically isolated $S = 1/2$ spin with $g = 2.0$. The

magnetic moment gradually decreases with a lowering of temperature, reaching the value of $0.11 \mu_B$ at 1.9 K, suggesting an antiferromagnetic interaction between the copper(II) ions. The magnetic data were analyzed by the molecular field approximation (Equation (1) [32]), for the Bleaney–Bowers Equation (2) [2] based on the Heisenberg model, $H = -2JS_1 \bullet S_2$, taking account of magnetic interaction between the neighboring dinuclear units as zJ' (z = number of interacting neighbors),

$$\chi_M' = \chi_M / \{1 - (2zJ' / Ng^2 \mu_B^2) \chi_M\} \quad (1)$$

$$\chi_M = (1 - p)(2Ng^2 \mu_B^2 / kT) [3 + \exp(-2J/kT)]^{-1} + pN\mu_B^2 g^2 / 2kT + 2N\alpha \quad (2)$$

where g is g value, J is an exchange coupling constant for the two copper(II) ions within the cluster, p = the fraction of mononuclear copper(II) impurity, and $N\alpha$ is the temperature-independent paramagnetism, which was set to be $60 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$ for each copper(II) ion [14]. The best-fitting parameters are $g = 2.16$, $2J = -272 \text{ cm}^{-1}$, $p = 0.0070$, and $zJ' = -5 \text{ cm}^{-1}$ as shown in Figure 8. The $2J$ value is comparable to those found in dinuclear copper(II) benzoate and its derivatives ($2J = -250$ – -350 cm^{-1}) [8,12,14,16,18,30,31,33]. It is known that there is a dependence of the magnetic coupling within the dinuclear cluster on the apical ligand species [34,35]. Considering for the apical ligand H_2O for **6**, the magnetic coupling within the dinuclear cluster of **6** can be regarded as relatively weak among the copper(II) benzoate analogues. The relatively weak antiferromagnetic interaction may be attributed to the bending of the benzoate moieties with the larger ϕ_{bend} angles of $5.9(4)$ and $1.9(3)^\circ$ in **6'**, which induces a poor overlap between the magnetic orbital and the $2p_x$ orbital of the benzoate oxygen atom, causing a suppression of the spin-exchange interaction via the benzoate-bridge [8,18]. The magnetic data for the complex **7** are shown in Figure 9 as the temperature variation of effective magnetic moment (μ_A) and magnetic susceptibility (χ_A) per mononuclear unit. The effective magnetic moment of **7** at 300 K is $1.91 \mu_B$ per the mononuclear unit. When cooling, the magnetic moment keeps constant until 20 K and steadily decreases from 20 to ca. 5 K, and then diminishes to a value of $1.69 \mu_B$ at 1.9 K, suggesting a weak antiferromagnetic interaction between the adjacent copper(II) ions. The crystal structure of **7** showed that the complex is essentially polynuclear copper(II) with an elongated octahedral geometry, where the axial μ -aqua-bonds with the distance of $2.3018(12) \text{ \AA}$ can be considered to intervene with the adjacent magnetic orbitals in the chain molecule. Therefore, magnetic interaction between the adjacent copper(II) ions was analyzed by the Bonner-Fisher equation (3) for an isolated Heisenberg 1D chain,

$$\chi_A = (Ng^2 \mu_B^2 / kT)(0.25 + 0.14995x + 0.30094x^2) / (1.0 + 1.9862x + 0.68854x^2 + 6.0626x^3) + N\alpha \quad (3)$$

in which $x = |J| / kT$ and J is the exchange integral for the two copper(II) ions, and the other symbols have their usual meanings [36]. The best fitting parameters are $g = 2.179(2)$ and $J = -0.21(1) \text{ cm}^{-1}$ with the fixed $N\alpha$ value of $60 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$. The J value in **7** is comparable to those of the μ -dicyanamido-bridged ($J = -0.02$ – -0.76 cm^{-1} , $\text{Cu} \cdots \text{Cu}$ 7.095– 8.314 \AA) [37], μ -croconato-bridged ($J = -0.06 \text{ cm}^{-1}$, $\text{Cu} \cdots \text{Cu}$ 7.6635 \AA [38]), μ - ClO_4 -bridged ($J = -0.41 \text{ cm}^{-1}$, $\text{Cu} \cdots \text{Cu}$ 6.9416 \AA [39]), μ -azido-bridged ($J = 1.68 \text{ cm}^{-1}$, $\text{Cu} \cdots \text{Cu}$ 5.7949 \AA ; $J = -3.82 \text{ cm}^{-1}$, $\text{Cu} \cdots \text{Cu}$ 3.550 \AA [40]) copper(II) chain compounds, confirming the very weak antiferromagnetic interaction. In **7**, the magnetic orbitals should lie in the equatorial plane involving the benzoate- and aqua- oxygen donors, and thus the superexchange interaction via the axial aqua-oxygen might be negligible. However, the superexchange interaction via the $\text{Cu-O-C-O} \cdots \text{H-O-H} \cdots \text{O-C-O-Cu}$ is possible, because of the hydrogen bonding between the non-coordinating oxygen atom of the monodentate benzoate ligand and the axial aqua-oxygen atom, resulting in the weak antiferromagnetic interaction.

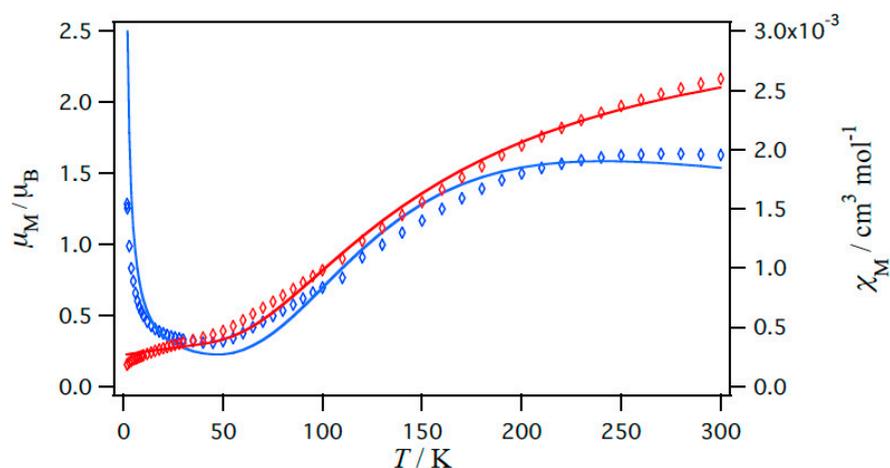


Figure 8. Temperature dependence of magnetic moments (red rhombuses) and magnetic susceptibilities (blue rhombuses) of $[\text{Cu}_2(234\text{-tmbz})_4(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ (6).

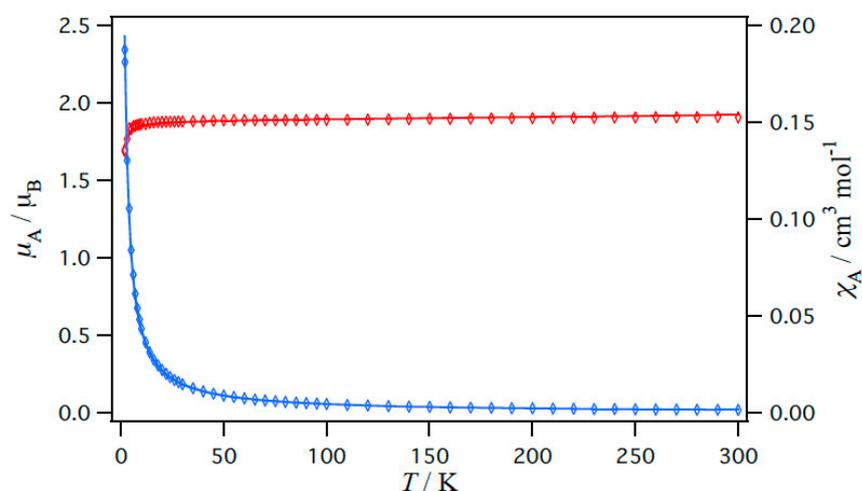


Figure 9. Temperature dependence of magnetic moments (red rhombuses) and magnetic susceptibilities (blue rhombuses) of $[\text{Cu}(246\text{-tmbz})_2(\text{H}_2\text{O})_4] \cdot \text{H}_2\text{O}$ (7).

2.6. Adsorption Properties of Copper(II) Carboxylate

We measured the adsorption property of **6** for N_2 to see if complex **6** has a porous structure or not. Intriguingly, the adsorption isotherm of N_2 at 77 K showed an adsorption property with the Type I behavior having a $125.4 \text{ m}^2 \text{g}^{-1}$ of specific surface area estimated from Langmuir plot as shown in Figure 10, meaning the existence of a uniform micropore in **6**. A t -plot analysis of the N_2 adsorption isotherm suggested a diameter of micropore to be 0.76 nm. If we refer to the crystal structure of **6'**, it seems to have almost no voids in the crystal. However, very narrow voids faced each other by the benzoate rings can be found in the crystal structure as shown in Figure 11. Similar narrow voids were found in the chain compound of dinuclear rhodium(II) benzoate with pyrazine, which is known as a porous material with the Type I adsorption isotherm for N_2 gas [41,42].

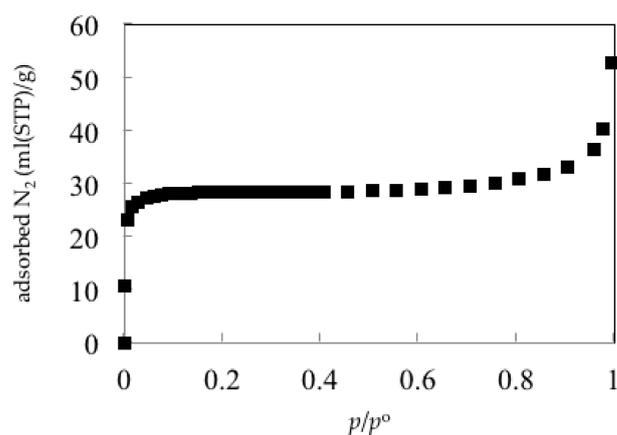


Figure 10. N_2 adsorption isotherm on **6**.

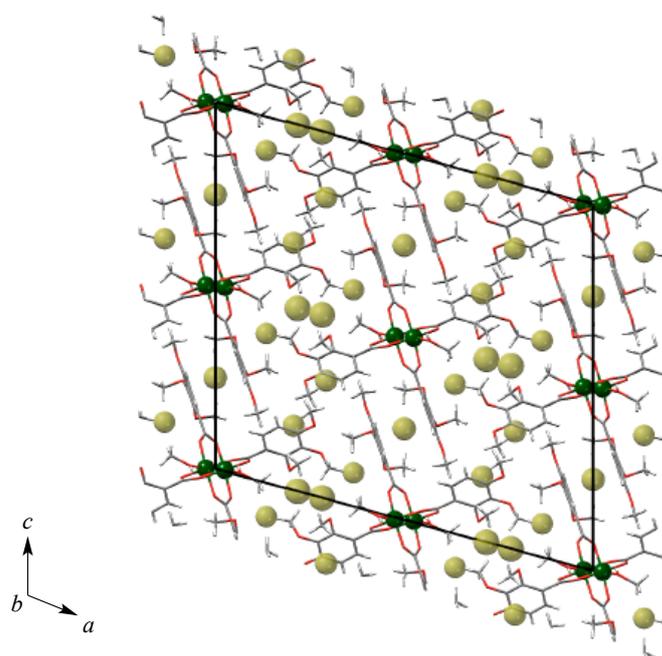


Figure 11. Packing diagram in the crystal structure of **6'**, showing narrow voids with a radius of 1.7 Å.

3. Materials and Methods

All the chemicals were commercial products and were used as supplied.

Synthesis of $[Cu_2(234\text{-tmbz})_4(H_2O)_2] \cdot H_2O$ (**6**). To a 5 cm³ of 0.10 M sodium hydroxide solution, a portion of 2,3,4-trimethoxybenzoic acid (507.9 mg, 2.39 mmol) was added. The solution was neutralized by adding nitric acid with phenolphthalein indicator. To the neutralized solution, a 5 cm³ of aqueous solution of copper(II) nitrate trihydrate (304.3 mg, 1.26 mmol) was added with stirring to give a pale blue precipitate. The precipitate was filtered off and desiccated in vacuo. Yield: 568.3 mg, 93.6%. Found C 46.38, H 4.28%. Calcd for C₄₀H₅₀Cu₂O₂₃: C 46.83, H 4.91%. IR (KBr, cm⁻¹): 3441(ν (OH)), 2994(ν (CH, ring)), 2941(ν_{as} (CH₃)), 2839(ν_s (CH₃)), 1602(ν_{as} (COO)), 1560, 1493(δ_{as} (CH₃)), 1468(ν_s (COO)), 1395(δ_s (CH₃)), 1289, 1226, 1095, 1025, 1001, 949, 887, 835, 810(δ (CH, ring)), 795, 763, 702, 656, 625. Diffuse reflectance spectra: λ_{max} 246, 286, 360sh, 706 nm. X-ray quality crystals $[Cu_2(234\text{-tmbz})_4(CH_3OH)_2]$ (**6'**) were grown by recrystallization from methanol at ambient temperature.

Synthesis of $[Cu(246\text{-tmbz})_2(\mu\text{-}H_2O)_2(H_2O)_2]_n \cdot nH_2O$ (**7**). To a 5 cm³ of 0.10 M sodium hydroxide solution, a portion of 2,4,6-trimethoxybenzoic acid (509.4 mg, 2.40 mmol) was

added. The solution was neutralized by adding nitric acid with phenolphthalein indicator. To the neutralized solution, a 5 cm³ of aqueous solution of copper(II) nitrate trihydrate (529.8 mg, 2.19 mmol) was added with stirring to give a green precipitate. The precipitate was filtered off and desiccated in vacuo. Yield: 530.8 mg, 50.2%. Found C 42.04, H 5.60%. Calcd for C₂₀H₃₂CuO₁₅: C 41.70, H 5.60%. IR (KBr, cm⁻¹): 3634(ν (OH)), 3538(ν (OH)), 3384(ν (OH)), 3120(ν (OH)), 3003(ν (CH, ring)), 2948(ν_{as} (CH₃)), 2840(ν_s (CH₃)), 1608(ν_{as} (COO)), 1538, 1459(δ_{as} (CH₃)), 1414(ν_s (COO)), 1385(δ_s (CH₃)), 1335, 1229, 1207, 1162, 1126, 1052, 951, 810(δ (CH, ring)), 652. Diffuse reflectance spectra: λ_{max} 212, 254, 310, 750 nm. X-ray quality crystals were grown by recrystallization from methanol at ambient temperature.

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 spectra were 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-7 SQUID susceptometer from 1.9 to 300 K with a static field of 0.5 T. The polycrystalline samples were ground into a fine powder, 47.47 mg of **6** and 17.07 mg of **7** of which, were used for the measurements. The susceptibilities were corrected for the diamagnetism of the constituent atoms using Pascal's constants [43]. Adsorption measurements for N₂ were performed using a MicrotracBEL BELSORP-mini II. Prior to the adsorption, the sample was evacuated at 298 K for 2 h.

Single-crystal diffraction data were measured on a Bruker Smart APEX CCD diffractometer equipped with a graphite crystal and incident beam monochromator using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The structures were solved by intrinsic phasing methods and refined by full-matrix least-squares methods. The hydrogen atoms were inserted at their calculated positions and fixed there, except for those attached to the methanol oxygen atom of **6** and water oxygen atoms of **7**, which were located from the D-Fourier maps. All of the calculations were carried out utilizing the SHELXTL software package [44]. Crystallographic data have been deposited with Cambridge Crystallographic Data Centre: Deposit numbers CCDC-1570723 and 2060931. Copies of the data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> (accessed on 4 February 2021). (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).

4. Conclusions

In this study, two new copper(II) carboxylates **6** and **7** were prepared by a reaction of copper(II) nitrate with 2,3,4-trimethoxybenzoic acid or 2,4,6-trimethoxybenzoic acid. The X-ray crystal structure analysis revealed that **6** is the *syn-syn*- μ -carboxylato-bridged dinuclear copper(II) cluster with an antiferromagnetic interaction and with Type I N₂-adsorption behavior having a 125.4 m²g⁻¹ of specific surface area, while **7** is not dinuclear cluster, but the μ -aqua-bridged copper(II) chain molecule, where the magnetic interaction via the μ -aqua bridge was found to be weak and antiferromagnetic. In the cases of 3,4,5-trimethoxybenzoic acid, 2,3,4-trimethoxybenzoic acid, and even more bulky 3,4,5-tri-O-benzylgalic acid, dinuclear copper(II) clusters were formed. Thus far, only in the case of 2,4,6-trimethoxybenzoic acid, the polynuclear copper(II) chain molecule was found for the first time here. Considering these results, the 2,4,6-trimethoxy groups of the benzoate ring should invoke a large rotation to the OCO plane because of the steric hindrance with the 2- and 6-methoxy groups of the benzoate rings to form the Cu(II) chain compound.

Author Contributions: M.M. conceived and designed the experiments, analyzed the data, and wrote the paper; C.Y., K.T., R.N., Y.A. and R.T. performed the experiments; D.Y. performed the crystallographic work; R.M. performed the crystallographic work and magnetic measurement; H.T. performed the adsorption measurement; M.H. and M.T. wrote the paper. All authors have read and agreed to the published version of the manuscript.

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References

1. Van Niekerk, J.N.; Schoening, F.R. A New Type of Copper Complex as found in the Crystal Structure of Cupric Acetate, $\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{H}_2\text{O}$. *Acta Crystallogr.* **1953**, *6*, 227–232. [[CrossRef](#)]
2. Bleaney, B.; Bowers, K.D. Anomalous paramagnetism of copper acetate. *Proc. Roy. Soc. Lond.* **1952**, *A214*, 451–465. [[CrossRef](#)]
3. Kato, N.; Jonassen, H.B.; Fanning, J.C. Copper(II) Complexes with Subnormal Magnetic Moments. *Chem. Rev.* **1964**, *64*, 99–128. [[CrossRef](#)]
4. Doedens, R.J. Structure and Metal-Metal Interactions in Copper(II) Carboxylate Complexes. *Prog. Inorg. Chem.* **1976**, *21*, 209–231.
5. Catterick, J.; Thornton, P. Structures and Physical Properties of Polynuclear Carboxylates. *Adv. Inorg. Chem. Radiochem.* **1977**, *20*, 291–362. [[CrossRef](#)]
6. Melnik, M. Study of the relation between the structural data and magnetic interaction in oxo-bridged binuclear copper(II) compounds. *Coord. Chem. Rev.* **1982**, *42*, 259–293. [[CrossRef](#)]
7. Kato, M.; Muto, Y. Factors affecting the magnetic properties of dimeric copper(II) complexes. *Coord. Chem. Rev.* **1988**, *92*, 45–83. [[CrossRef](#)]
8. Kawata, T.; Uekusa, H.; Ohba, S.; Furukawa, T.; Tokii, T.; Muto, Y. Magneto-Structural Correlation in Dimeric Copper(II) Benzoates. *Acta Crystallogr. Part. B* **1992**, *48*, 253–261. [[CrossRef](#)]
9. Sundberg, M.R.; Uggla, R.; Melnik, M. Comparison of the structural parameters in copper(II) acetate-type dimers containing distorted square pyramidal Cu_4O and CuO_4N chromophores. *Polyhedron* **1996**, *15*, 1157–1163. [[CrossRef](#)]
10. Valach, F.; Melnik, M.; Bernardinelli, G.; Fromm, K.M. A structural study of copper(II) carboxylates: Crystal structure and physical characterization of $[\text{Cu}_2(2\text{-bromopropionato})_4(\text{caffeine})_2]$. *J. Chem. Crystallogr.* **2006**, *36*, 571–580. [[CrossRef](#)]
11. Mikuriya, M. Copper(II) Acetate as a Motif of Metal-Assembled complexes. *Bull. Jpn. Soc. Coord. Chem.* **2008**, *52*, 17–28. [[CrossRef](#)]
12. Nukada, R.; Mori, W.; Takamizawa, S.; Mikuriya, M.; Handa, M.; Naono, H. Microporous Structure of a Chain Compound of Copper(II) Benzoate Bridged by Pyrazine. *Chem. Lett.* **1999**, *28*, 367–368. [[CrossRef](#)]
13. Nukada, R.; Mikuriya, M.; Handa, M.; Naono, H. Hydrophobic micropore in a chain compound of dinuclear copper(II) benzoate with pyrazine—Adsorption properties for N_2 , CCl_4 , H_2O , CO_2 , and CH_3CN . In *Proceedings of the 2nd International Porous and Powder Materials Symposium and Exhibition PPM 2015, Izmir, Turkey, 15–18 September 2015*; Ozdemir, S.K., Polat, M., Tanoglu, M., Eds.; The Organizing Committee of The International Porous and Power Materials Symposium and Exhibition, Uc Adim Printing House: Izmir, Turkey, 2015; pp. 77–81. ISBN 978-975-6590-07-2.
14. Horikoshi, R.; Mikuriya, M. One-Dimensional Coordination Polymers from the Self-Assembly of Copper(II) Carboxylates and 4,4'-Dithiobis(pyridine). *Bull. Chem. Soc. Jpn.* **2005**, *78*, 827–834. [[CrossRef](#)]
15. Wada, S.; Yoshioka, D.; Mikuriya, M. Synthesis, Crystal Structures, and Magnetic Properties of Dinuclear and Hexanuclear Copper(II) Complexes with Cyclam-based Macrocyclic Ligands Having Four Schiff-Base Pendant Arms. *Bull. Chem. Soc. Jpn.* **2010**, *83*, 364–374. [[CrossRef](#)]
16. Mikuriya, M.; Yamakawa, C.; Tanabe, K.; Yoshioka, D.; Mitsuhashi, R.; Tanaka, H.; Handa, M. Synthesis, crystal structure, magnetic property, and N_2 -gas-adsorption property of dinuclear copper(II) 3,4,5-trimethoxybenzoate. *J. Turk. Chem. Soc. Sect. A* **2018**, *5*, 103–110. [[CrossRef](#)]
17. Mikuriya, M.; Indrawati, R.; Hashido, R.; Matsubara, S.; Nakamura, C.; Yoshioka, D.; Yokota, K.; Fukuzaki, M.; Handa, M. Chain Compounds Based on Paddle-wheel Copper(II) Carboxylate Bearing Four Nitroxide Radicals. *Magnetochemistry* **2018**, *4*, 22. [[CrossRef](#)]
18. Mikuriya, M.; Yamakawa, C.; Masuda, N.; Yoshioka, D.; Yamaguchi, S.; Yamada, H.; Mizuta, T.; Kawata, N.; Tanaka, H.; Handa, M. Dinuclear Copper(II) 3,4,5-Tri-O-benzylgallate. *Open Chem. J.* **2019**, *6*, 19–26. [[CrossRef](#)]
19. Ishida, H.; Handa, M.; Mikuriya, M. Synthesis and Crystal Structure of Aqua Adduct of Dinuclear Ruthenium(II,III) 3,4,5-Tri(ethoxy-d₅)benzoate Tetrafluoroborate. *X-ray Struct. Anal. Online* **2014**, *30*, 9–10. [[CrossRef](#)]
20. Ishida, H.; Handa, M.; Ikeue, T.; Taguchi, J.; Mikuriya, M. Synthesis, crystal structure, and ^1H NMR spectra of chlorido-bridged chain complex of dinuclear ruthenium(II,III) 3,4,5-tri(ethoxy-d₅)benzoate. *Chem. Pap.* **2010**, *64*, 767–775. [[CrossRef](#)]

21. Ishida, H.; Handa, M.; Hiromitsu, I.; Ujiie, S.; Yoshioka, D.; Mitsuhashi, R.; Mikuriya, M. Magnetic and liquid-crystalline properties of chlorido- and cyanato-bridged chain complexes of mixed-valent dinuclear ruthenium(II,III) 3,4,5-trialkoxybenzoates. *New J. Chem.* **2019**, *43*, 1134–1145. [[CrossRef](#)]
22. Ishida, H.; Handa, M.; Hiromitsu, I.; Mikuriya, M. Fastener effect on magnetic properties of chain compounds of dinuclear ruthenium carboxylates. *Chem. Pap.* **2013**, *67*, 743–750. [[CrossRef](#)]
23. Nakamoto, K. *Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B*, 6th ed.; John Wiley & Sons: Hoboken, NJ, USA, 2009; pp. 64–67. ISBN 978-0-471-74493-1.
24. Ferraro, J.R.; Walker, W.R. Infrared Spectra of Hydroxy-Bridged Copper(II) Compounds. *Inorg. Chem.* **1965**, *4*, 1382–1386. [[CrossRef](#)]
25. Chaudhuri, P.; Ventur, D.; Wiegardt, K.; Peters, E.-M.; Peters, K.; Simon, A. Preparation, Magnetism, and Crystal Structures of the Tautomers $[L(\text{Cu}(\mu_2\text{-OH})_2\text{CuL})(\text{ClO}_4)_2]$ (Blue) and $[L\text{Cu}(\mu_2\text{-OH}_2)(\mu_2\text{-O})\text{CuL}](\text{ClO}_4)_2$ (Green): μ -Aqua- μ -oxo vs. Di- μ -hydroxo Linkage. *Angew. Chem. Int. Ed. Engl.* **1983**, *24*, 57–59. [[CrossRef](#)]
26. Nakanishi, K.; Solomon, P.H.; Furutachi, N. *Infrared Absorption Spectroscopy*; Nankodo: Tokyo, Japan, 1978. (In Japanese)
27. Murakami, Y.; Sakata, K. *Kireto Kagaku*; Ueno, K., Ed.; Nankodo: Tokyo, Japan, 1976; Volume 1, pp. 91–396. (In Japanese)
28. Todaro, M.; Sciortino, L.; Gelardi, F.M.; Buscarino, G. Determination of Geometry Arrangement of Copper Ions in HKUST-1 by XAFS During a Prolonged Exposure to Air. *J. Phys. Chem. C* **2017**, *121*, 24853–24860. [[CrossRef](#)]
29. Scatena, R.; Guntern, Y.T.; Macchi, P. Electron Density and Dielectric Properties of Highly Porous MOFs: Binding and Mobility of Guest Molecules in $\text{Cu}_3(\text{BTC})_2$ and $\text{Zn}_3(\text{BTC})_2$. *J. Am. Chem. Soc.* **2019**, *141*, 9382–9390. [[CrossRef](#)] [[PubMed](#)]
30. Erre, L.S.; Micera, G.; Piu, P.; Cariati, F.; Ciani, G. Interaction of metal ions with humic acid-like models. Part 4. Synthesis, spectral properties, and crystal and molecular structure of tetrakis(μ -2,6-dimethoxybenzoato)diaquodicopper(II) and of bis(μ -2,6-dimethoxybenzoato)bis(μ -acetato)diaquodicopper(II), a case of a dimeric copper(II) carboxylate complex with mixed bridges. *Inorg. Chem.* **1985**, *24*, 2297–2300. [[CrossRef](#)]
31. Harrison, W.; Rettig, S.; Trotter, J. Crystal and molecular structure of tetra- μ -O-bromobenzoato-bis[aquocopper(II)]. *J. Chem. Soc. Dalton Trans.* **1972**, 1852–1856. [[CrossRef](#)]
32. O'Connor, C.J. Magnetochemistry—Advances in Theory and Experimentation. *Prog. Inorg. Chem.* **1982**, *29*, 205–283. [[CrossRef](#)]
33. Lewis, J.; Mabbs, F.E.; Royston, L.K.; Smail, W.R. The preparation, magnetic susceptibilities, and electron resonance of some copper(II) carboxylate compounds. *J. Chem. Soc. A* **1969**, 291–296. [[CrossRef](#)]
34. Zhang, X.X.; Chui, S.S.-Y.; Williams, I.D. Cooperative magnetic behavior in the coordination polymers $[\text{Cu}_3(\text{TMA})_2\text{L}_3]$ (L = H_2O , pyridine). *J. Appl. Phys.* **2000**, *87*, 6007–6009. [[CrossRef](#)]
35. Da Silva, G.G.; Machado, F.L.A.; Junior, S.A.; Padron-Hernandez, E. Metal-organic framework: Structure and magnetic properties of $[\text{Cu}_3(\text{BTC})_2(\text{L})_x \cdot (\text{CuO})_y]_n$ (L = H_2O , DMF). *J. Solid State Chem.* **2017**, *253*, 1–5. [[CrossRef](#)]
36. Bonner, J.C.; Fisher, M.E. Linear Magnetic Chains with Anisotropic Coupling. *Phys. Rev.* **1964**, *135*, A640–A658. [[CrossRef](#)]
37. Mautner, F.A.; Mikuriya, M.; Ishida, H.; Sakiyama, H.; Louka, F.R.; Humphrey, J.W.; Massoud, S.S. Dicyanamido-metal(II) complexes. Part 4: Synthesis, structure and magnetic characterization of polynuclear Cu(II) and Ni(II) complexes bridged by μ -1,5-dicyanamide. *Inorg. Chim. Acta* **2009**, *362*, 4073–4080. [[CrossRef](#)]
38. Massoud, S.S.; Vicente, R.; Fontenot, P.R.; Gallo, A.A.; Mikuriya, M.; Albering, J.H.; Mautner, F.A. Polynuclear croconato-bridged-copper(II) complexes derived from tri- and tetra-dentate amines. *Polyhedron* **2012**, *46*, 66–73. [[CrossRef](#)]
39. Mautner, F.A.; Koikawa, M.; Mikuriya, M.; Harrelson, E.V.; Massoud, S.S. Copper(II)-azido complexes constructed from polypyridyl amine ligands. *Polyhedron* **2013**, *59*, 17–22. [[CrossRef](#)]
40. Louka, F.R.; Massoud, S.S.; Haq, T.K.; Koikawa, M.; Mikuriya, M.; Omote, M.; Fischer, R.C.; Mautner, F.A. Synthesis, structural characterization and magnetic properties of one-dimensional Cu(II)-azido coordination polymers. *Polyhedron* **2017**, *138*, 177–184. [[CrossRef](#)]
41. Mikuriya, M.; Higashiguchi, M.; Sakai, T.; Yoshioka, D.; Handa, M. Chain compounds of rhodium(II) benzoate bridged by N,N' -didentate ligands. In *Progress in Coordination and Bioinorganic Chemistry*; Melnik, M., Sirota, A., Eds.; Slovak Technical University Press: Bratislava, Slovakia, 2003; pp. 213–218.
42. Takamizawa, S.; Hiroki, T.; Nakata, E.; Mochizuki, K.; Mori, W. Crystal Structure and Gas Adsorption Property of Rhodium(II) Benzoate Pyrazine. *Chem. Lett.* **2002**, *31*, 1208–1209. [[CrossRef](#)]
43. Kahn, O. *Molecular Magnetism*; VCH Publications: New York, NY, USA, 1993; pp. 3–4. ISBN 1-56081-566-3.
44. Sheldrick, G.M. A short history of SHELX. *Acta Crystallogr. Sect. A* **2008**, *64*, 112–122. [[CrossRef](#)] [[PubMed](#)]