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Catalytic transesterification reactions of one-dimensional coordination polymers containing paddle-wheel-type units connected by various bridging ligands

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ABSTRACT

The paddle-wheel dinuclear unit consists of two Cu^{II} ions bridged by four benzoate ligands, and these paddle-wheel $[Cu_2(O_2CPh)_4]$ units are connected by various bridging ligands to form one-dimensional chained compounds formulated as $[Cu_2(O_2CPh)_4(\mu\text{-L})]$ (L = 2,4-bpe (**1**), 3,3′-dipicam (**3**), 2,5-Me_2pyz (**4**), pyz (**5**), 4,4′-bpy (**6**), and 4-pds (**7**)). The compound **2**, formulated as $[[Cu_2(O_2CPh)_4][Cu(O_2CPh)_2](\mu\text{-bpp})_2]$, consists of alternating units of $[Cu_2(O_2CPh)_4]$ and $[Cu(O_2CPh)_2]$ connected by via bpp. Compounds **1–5** and **7** efficiently catalyzed the transesterification of a variety of esters, while it has been reported that Cu-containing complexes or coordination polymers do not usually show catalytic activities for the transesterification reactions. Among these compounds, **2** was most effective. It has been proposed that in the transesterification reaction, a mononuclear type of Cu complex might be the major species of compound **2** in solution, while for all other compounds, a paddle-wheel unit might be the major reactive species.

1. Introduction

The construction of coordination networks via self-assembly processes has attracted considerable attention in the fields of supramolecular chemistry and crystal engineering [1–5] because such coordination networks have an intriguing variety of topologies, structural diversity, and potential applications as functional materials [6–16]. Much effort has been devoted to the study of fundamental structural aspects to understand and control several factors that affect the self-assembly of coordination networks. These factors are the coordination geometry of metal ions [17,18], the structure of organic ligands [19–22], hydrogen bonding [23–32], π–π stacking [4], counter-anions [33–37], pH values [38,39], temperature [40,41], the ligand-to-metal ratio [42,43], the solvent system [44–48], and the template effect [49]. A subtle change in any of these factors can lead to new complexes with different structural topologies and different functions. Therefore, there is a need for greater understanding of the factors because their rational controls produce the desired topologies with specific properties.

We have recently shown that the assembly process of zinc benzoates is highly influenced by the types of bridging ligands used [50]. Assembly of zinc(II)–benzoate with different types of pyrazine gives different structures ranging from dinuclear, trinuclear, and pentanuclear complexes to one-dimensional (1-D) and two-dimensional (2-D) coordination polymers. Moreover, we have further observed the various complex formations (0-D, 1-D, and 2-D) of manganese(II)–benzoates with various bridging ligands, such as pyrazine (pyz), 4,4′-bipyridine (4,4′-bpy), 3,3′-dipicoylamine (3,3′-dpicam), 3-methylisoquinoline, and 4,4′-dithiopyridine (4,4′-dtp) [51]. These observations led us to perform a systematic investigation of the relationships between the Cu–benzoate unit and the nature of the ligands because such a factor was seldom systematically considered in the assembly of Cu(benzoate)$_2$-containing coordination polymers.

We report herein the syntheses, structures, and reactivities of the Cu–benzoate unit with various bridging ligands. The Cu–benzoate system afforded predominantly 1-D coordination polymers with a paddle-wheel building block unit. Importantly, compounds **1–5** and **7** efficiently catalyzed the transesterification reaction of a variety of esters, while it has been reported that Cu-containing complexes or coordination polymers do not usually show catalytic activities for the transesterification reactions.

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2. Experimental

2.1. Materials

$Cu(NO_3)_2 \cdot H_2O$, $C_6H_5COONH_4$, trans-1-(2-pyridyl)-2-(4-pyridyl)ethylene, pyrazine, 4,4′-trimethylene dipyridine, 3,3′-dipicoylamine, 2,5-dimethylpyrazine, 4-nitrophenyl acetate, phenyl acetate, 4-methylphenyl acetate, 4-nitrophenyl benzoate, phenyl benzoate, 4-chlorophenyl benzoate, 4-methylphenyl benzoate, vinyl acetate, methylacetate, methylbenzoate, methylene chloride, tetrahydrofuran and methanol were purchased from Aldrich and were used as received. 4-Fluorophenyl acetate and 4-nitrophenyl benzoate were obtained from Lancaster.

2.2. Instrumentation

Elemental analysis for carbon, nitrogen, and hydrogen was performed using a vario MACRO (Elemental Analysensysteme, Germany) in the Laboratory Center of Seoul National University of Science and Technology, Korea. IR spectra were measured on a BIO RAD FTS 135 spectrometer as KBr pellets. Thermogravimetric analyses (TGA) were performed on a Shimadzu TA50 integration thermal analyzer. Product analysis for the transesterification reaction was performed on either a Hewlett–Packard 5890 II Plus gas chromatograph interfaced with a Hewlett–Packard Model 5989B mass spectrometer or on a Donam Systems 6200 gas chromatograph equipped with a FID detector using a 30-m capillary column (Hewlett–Packard, HP-1, HP-5, and Ultra 2). Electrospray ionization mass spectra (ESI-MS) were collected by manually infusing samples directly into the source. The spray voltage was set at 4.2 kV and the capillary temperature at 80 °C.

2.3. Synthesis of $[[Cu_2(O_2CPh)_4(\mu\text{-}2,4\text{-bpe})]\cdot(THF)]_n$ (**1**)

trans-1-(2-Pyridyl)-2-(4-pyridyl)ethylene (37.6 mg, 0.2 mmol) was dissolved in 4 mL tetrahydrofuran and carefully layered with 4 mL of a methanol solution of $Cu(NO_3)_2 \cdot H_2O$ (23.7 mg, 0.1 mmol) and $C_6H_5COONH_4$ (28.4 mg, 0.2 mmol). Blue block crystals of compound **1** suitable for X-ray analysis were obtained in 2 weeks. The yield was 27.8 mg (32.1%) based on metal for compound **1**. The purity of the bulk sample was checked by powder XRD (Fig. S1). IR (KBr): $\nu(\text{cm}^{-1})$ = 1619(m), 1570(m), 1484(w), 1396(s), 1101(w), 1068(w), 1025(w), 842(w), 711(s). *Anal.* Calc. for $C_{44}H_{38}Cu_2N_2O_9$ (865.84), **1**: C, 60.98; H, 4.43; N, 3.24. Found: C, 60.58; H, 4.63; N, 3.11%.

2.4. Synthesis of $[[Cu_2(O_2CPh)_4][Cu(O_2CPh)_2](\mu\text{-bpp})_2]_n$ (**2**)

4,4′-Trimethylene dipyridine (40.5 mg, 0.2 mmol) was dissolved in 4 mL tetrahydrofuran and carefully layered with 4 mL of a methanol solution of $Cu(NO_3)_2 \cdot H_2O$ (23.7 mg, 0.1 mmol) and $C_6H_5COONH_4$ (28.4 mg, 0.2 mmol). Blue block crystals of compound **2** suitable for X-ray analysis were obtained in a week. The yield was 21.2 mg (16.14%) based on metal for compound **2**. The purity of the bulk sample was checked by powder XRD (Fig. S2). IR (KBr): $\nu(\text{cm}^{-1})$ = 1614(m), 1569(m), 1499(w), 1398(s), 1351(m), 1221(w), 1067(w), 822(w), 714(s), 683(s). *Anal.* Calc. for $C_{68}H_{58}Cu_3N_4O_{12}$ (1313.80), **2**: C, 62.16; H, 4.46; N, 4.47. Found: C, 62.48; H, 4.52; N, 4.12%.

2.5. Synthesis of $[[Cu_2(O_2CPh)_4](\mu\text{-}3,3'\text{-dipicam})]_n$ (**3**)

3,3′-Dipicoylamine (36.7 μL, 0.2 mmol) was dissolved in 4 mL methylene chloride and carefully layered with 4 mL of a methanol solution of $Cu(NO_3)_2 \cdot H_2O$ (23.7 mg, 0.1 mmol) and $C_6H_5COONH_4$ (28.4 mg, 0.2 mmol). Blue block crystals of compound **3** suitable for X-ray analysis were obtained in 2 weeks. The yield was 17.2 mg (21.2%) based on metal for compound **3**. The purity of the bulk sample was checked by powder XRD (Fig. S3). IR (KBr): $\nu(\text{cm}^{-1})$ = 1610(m), 1567(m), 1479(w), 1398(s), 1063(w), 1021(w), 969(w), 841(w), 814(w), 715(s), 683(s). *Anal.* Calc. for $C_{40}H_{33}Cu_2N_3O$ (810.77), **3**: C, 59.25; H, 4.11; N, 5.18. Found: C, 59.43; H, 4.10; N, 5.37%.

2.6. Synthesis of $[[Cu_2(O_2CPh)_4(\mu\text{-}2,5\text{-}Me_2pyz)]\cdot 2(H_2O)]_n$ (**4**)

2,5-Dimethylpyrazine (21.8 mg, 0.2 mmol) was dissolved in 4 mL methylene chloride and carefully layered with 4 mL of a methanol solution of $Cu(NO_3)_2 \cdot H_2O$ (23.7 mg, 0.1 mmol) and $C_6H_5COONH_4$ (28.4 mg, 0.2 mmol). Blue rod-type crystals of compound **4** suitable for X-ray analysis were obtained in 10 days. The yield was 31.7 mg (40.0%) based on metal for compound **4**. The purity of the bulk sample was checked by powder XRD (Fig. S4). IR (KBr): $\nu(\text{cm}^{-1})$ = 1613(m), 1570(m), 1494(w), 1403(s), 1334(w), 1064(w), 1026(w), 843(w), 715(s), 683(s). *Anal.* Calc. for $C_{34}H_{36}Cu_2N_2O_{12}$ (791.74), **5**: C, 51.58; H, 4.59; N, 3.54. Found: C, 51.85; H, 4.01; N, 3.72%.

2.7. Synthesis of $[[Cu_2(O_2CPh)_4(\mu\text{-pyz})]\cdot 2(CH_2Cl_2)]_n$ (**5**)

Pyrazine (16.2 mg, 0.2 mmol) was dissolved in 4 mL methylene chloride and carefully layered with 4 mL of a methanol solution of $Cu(NO_3)_2 \cdot H_2O$ (23.7 mg, 0.1 mmol) and $C_6H_5COONH_4$ (28.4 mg, 0.2 mmol). Blue plate crystals of compound **5** suitable for X-ray analysis were obtained in 2 weeks. The yield was 23.2 mg (26.9%) based on metal for compound **5**. The purity of the bulk sample was checked by powder XRD (Fig. S5). IR (KBr): $\nu(\text{cm}^{-1})$ = 1614(m), 1570(m), 1402(s), 1050(w), 1025(w), 844(w), 802(w), 716(m), 684(m). *Anal.* Calc. for $C_{34}H_{28}Cl_4Cu_2N_2O_8$ (861.46), **5**: C, 47.40; H, 3.28; N, 3.25. Found: C, 47.03; H, 3.44; N, 2.85%.

2.8. Synthesis of $[[Cu_2(O_2CPh)_4(\mu\text{-4pds})]\cdot 0.5(CH_3OH)]_n$ (**7**)

Compound **7** was synthesized by a modified procedure [52]. 4,4′-Dithiopyridine (45.4 mg, 0.2 mmol) was dissolved in 4 mL of methylene chloride and carefully layered with 4 mL of a methanol solution of $Cu(NO_3)_2 \cdot H_2O$ (23.7 mg, 0.1 mmol) and $C_6H_5COONH_4$ (28.4 mg, 0.2 mmol). Blue plate crystals of compound **7** suitable for X-ray analysis were obtained in a week. The yield was 25.1 mg (29.7%) based on metal for compound **7**. IR (KBr): $\nu(\text{cm}^{-1)}$ = 1615 (m), 1571(m), 1481(w), 1397(s), 1220(w), 1066(w), 1024(w), 843(w), 708(s), 684(s). *Anal.* Calc. for $C_{38.5}H_{28}Cu_2N_2O_{8.5}S_2$ (845.83), **7**: C, 54.67; H, 3.34; N, 3.31. Found: C, 54.61; H, 2.97; N, 3.42%.

2.9. Catalytic activity of compounds **1**–**5** and **7**

Catalytic reaction conditions: The ester (0.05 mmol) was dissolved in methanol (1 mL), one of the compounds **1**–**5** or **7** (1.0 mg, 1.15×10^{-3} mmol for **1**, 2.0 mg, 1.14×10^{-3} mmol for **2**, 1.0 mg, 1.23×10^{-3} mmol for **3**, 1.0 mg, 1.26×10^{-3} mmol for **4**, 1.0 mg, 1.16×10^{-3} mmol for **5**, and 1.0 mg, 1.20×10^{-3} mmol for **7**) was added, and the resulting solution was shaken at 50 °C (450 rpm). The reaction conversion was monitored by GC/mass analysis of 20 μL aliquots drawn periodically from the reaction mixture. All reactions were run at least three times, and the average conversion yields are presented. Yields are based on the formation of the products, methylacetate or methylbenzoate.

2.10. Crystallography

The diffraction data for all six compounds were collected on a Bruker SMART AXS diffractometer equipped with a monochromator in the Mo Kα (λ = 0.71073 Å) incident beam. The crystal was mounted on a glass fiber. The CCD data were integrated and scaled using the BRUKER-SAINT software package, and the structure was solved and refined using SHEXTL V6.12 [53]. All hydrogen atoms except the hydrogen atoms of water molecules were located in the calculated positions. The crystallographic data for compounds **1**–**5** and the previously reported compounds **6** and **7** are listed in Table 1. Structural information was deposited at the Cambridge Crystallographic Data Center (CCDC reference numbers: CCDC 858917 for **1**, 858918 for **2**, 858919 for **3**, 858920 for **4**, and 858921 for **5**).

3. Results and discussion

The paddle-wheel-type Cu_2 units were connected by various bridging ligands to form one-dimensional chains. All five structures were determined by X-ray crystallography. The structures of all five compounds containing paddle-wheel Cu_2 units are shown in Scheme 1. The previously reported crystal structures of compounds **6** [18] and **7** [52] are also shown in Scheme 1 for comparison.

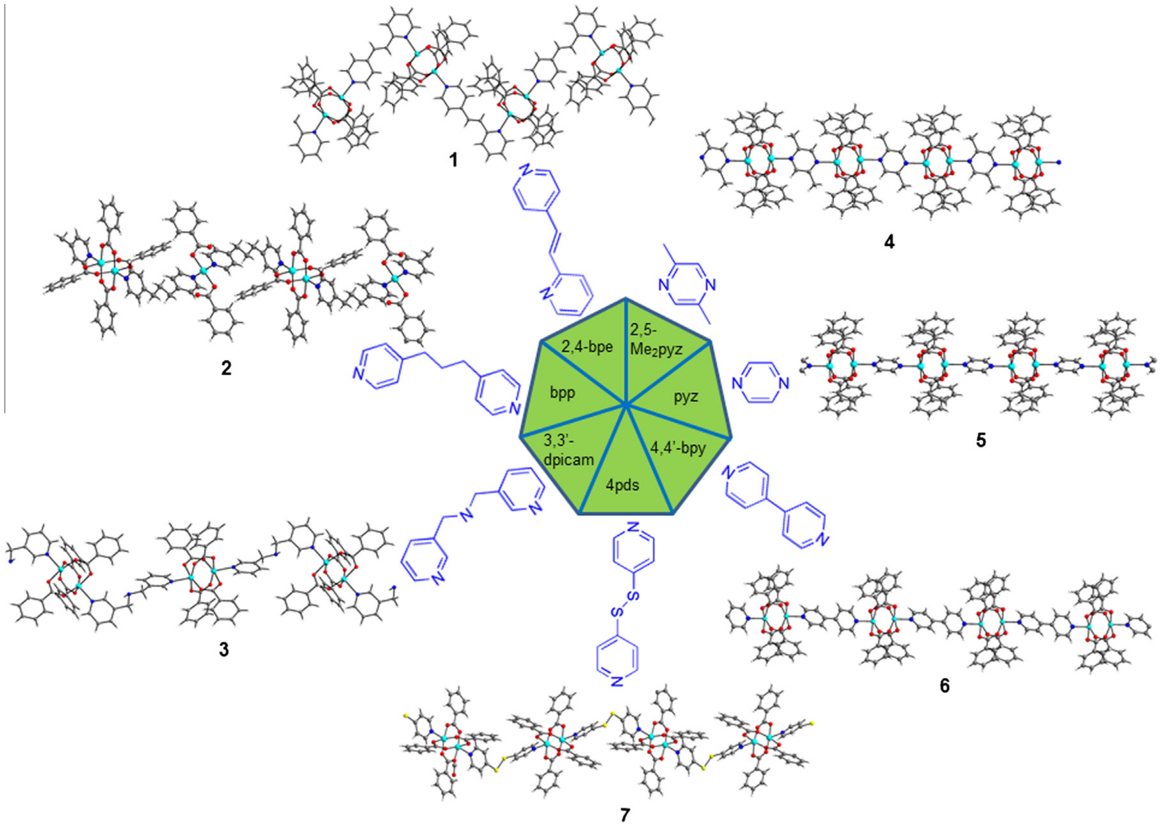
The paddle-wheel dinuclear unit consists of two Cu^{II} ions bridged by four benzoate ligands, and these paddle-wheel $[Cu_2(O_2CPh)_4]$ units are connected by various bridging ligands to form one-dimensional chained compounds formulated as $[Cu_2(O_2CPh)_4(\mu\text{-}2,4\text{-bpe})]\cdot(THF)$ (**1**) (Fig. 1), $[Cu_2(O_2CPh)_4(\mu\text{-}3,3'\text{-dipicam})]$ (**3**), $[Cu_2(O_2CPh)_4(\mu\text{-}2,5\text{-}Me_2pyz)]\cdot 2(H_2O)$ (**4**), $[Cu_2(O_2CPh)_4(\mu\text{-pyz})]\cdot 2(CH_2Cl_2)$ (**5**), $[Cu_2(O_2CPh)_4(\mu\text{-}4,4'\text{-bpy})]$ (**6**) [18], and $[Cu_2(O_2CPh)_4(\mu\text{-}4\text{-pds})]\cdot 0.5(CH_3OH)$ (**7**) [52] (2,4-bpe = *trans*-2(2-pyridyl)2-(4-pyridyl)ethylene, 3,3′-dipicam = 3,3′-dipicolylamine, 2,5-Me_2pyz = 2,5-dimethylpyrazine, pyz = pyrazine, 4,4′-bpy = 4,4′-bipyridine, and 4pds = 4,4′-dithiobis(pyridine). Compound **2**, formulated as $[Cu_2(O_2CPh)_4][Cu(O_2CPh)_2](\mu\text{-bpp})_2]$ (bpp = 1,3-bis(pyridyl)propane), consists of alternating units of $[Cu_2(O_2CPh)_4]$ and $[Cu(O_2CPh)_2]$ connected by bpp (Fig. 2). The elongation of the Cu–N bond distances of 2.1–2. 2 Å in all five new compounds relative to the typical Cu–N distance (ca. 2.0 Å) is due to a Jahn–Teller distortion of the copper(II) ion (Table 2); similar elongations are observed in related chain compounds of copper(II) carboxylates [54,55].

As we have previously reported, the construction of the crystal structures of zinc-benzoate compounds was strongly affected by the types of bridging pyrazine ligands used [50]. Simple pyrazine and 2,5-dimethlpyrazine produced two-dimensional and one-dimensional polymeric compounds, respectively. The other quinoxaline and two dimethyl-substituted pyrazine ligands gave dinuclear, trinuclear, and pentanuclear complexes. We have also found that the bridging bipyridyl ligands play very important roles in the construction of manganese(II)–benzoate coordination polymers [51]. The bridging bipyridyl ligands produced 1-D or 2-D polymeric manganese(II)–benzoate compounds. The pyz produced a Mn_6 cluster molecule, and 3-methylisoquinoline yielded a

Table 1
Crystallographic data for compounds **1**–**7**.

	1	**2**	**3**	**4**	**5**	**6**[a]	**7**[b]
Empirical formula	$C_{44}H_{38}Cu_2N_2O_9$	$C_{68}H_{58}Cu_3N_4O_{12}$	$C_{40}H_{33}Cu_2N_3O_8$	$C_{34}H_{28}Cu_2N_2O_{12}$	$C_{34}H_{28}Cl_4Cu_2N_2O_8$	$C_{38}H_{28}Cu_2N_2O_8$	$C_{38.5}H_{28}Cu_2N_2O_{8.5}S_2$
Formula weight	865.84	1313.80	810.77	783.66	861.46	767.72	845.83
T (K)	170(2)	293(2)	170(2)	293(2)	293(2)	170(2)	293(2)
λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073	0.71073
Space group	$P2_1/c$	$P\bar{1}$	$P\bar{1}$	$P2_1/c$	$P\bar{1}$	$C2/c$	$P\bar{1}$
a (Å)	10.4155(16)	9.8178(10)	10.299(6)	11.104(2)	9.7440(19)	20.3982(18)	10.382(2)
b (Å)	20.113(3)	10.7740(11)	10.846(6)	9.780(2)	10.039(2)	18.9865(16)	10.868(2)
c (Å)	19.323(3)	14.9306(15)	16.531(9)	18.453(4)	10.740(2)	21.4028(18)	17.793(4)
α (°)	90.00	79.685(2)	75.827(10)	90.00	89.94(3)	90.00	107.27(3)
β (°)	104.032(3)	81.615(2)	86.068(10)	97.12(3)	83.54(3)	118.152(2)	90.28(3)
γ (°)	90.00	78.697(2)	88.446(9)	90.00	62.30(3)	90.00	91.67(3)
V (Å^3)	3927.1(10)	1513.6(3)	1786.1(17)	1988.5(7)	922.7(3)	7308.5(11)	1916.1(7)
Z	4	1	2	2	1	8	2
D_{calc} (Mg/m^3)	1.464	1.441	1.508	1.309	1.550	1.425	1.466
Absorption coefficient (mm^{-1})	1.143	1.112	1.250	1.126	1.493	1.220	1.273
Crystal size (mm)	0.15 × 0.08 × 0.05	0.08 × 0.05 × 0.05	0.08 × 0.05 × 0.05	0.15 × 0.05 × 0.02	0.35 × 0.30 × 0.03	0.10 × 0.08 × 0.08	0.10 × 0.05 × 0.02
Reflections collected	19,821	8547	8855	10017	5185	20023	10074
Independent reflections (R_{int})	7470 (0.0618)	5820 (0.0272)	6124 (0.0784)	3751 (0.0667)	3541 (0.0257)	7123 (0.0589)	7137 (0.0811)
Data/restraints/parameters	7470/0/511	5820/0/394	6124/1/482	3751/0/227	3541/0/226	7123/0/461	7137/1/405
Goodness-of-fit (GOF) on F^2	0.900	1.053	0.759	0.967	0.943	0.945	0.796
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0420, wR_2 = 0.1141	R_1 = 0.0560, wR_2 = 0.1298	R_1 = 0.0609, wR_2 = 0.1221	R_1 = 0.0733, wR_2 = 0.1722	R_1 = 0.0499, wR_2 = 0.1208	R_1 = 0.0570, wR_2 = 0.1517	R_1 = 0.0961, wR_2 = 0.2393
R indices (all data)	R_1 = 0.0726, wR_2 = 0.1298	R_1 = 0.1016, wR_2 = 0.1445	R_1 = 0.1633, wR_2 = 0.1440	R_1 = 0.1279, wR_2 = 0.2031	R_1 = 0.0708, wR_2 = 0.1281	R_1 = 0.0852, wR_2 = 0.1578	R_1 = 0.2127, wR_2 = 0.2982
Largest difference peak and hole (e Å^{-3})	0.492 and −0.832	0.432 and −0.722	0.818 and −0.900	1.331 and −0.537	0.668 and −0.537	2.361 and −0.885	1.220 and −1.230

[a] See Ref. [18].
[b] See Ref. [52].



Scheme 1. Structures of compounds containing paddle-wheel-type Cu_2 units.

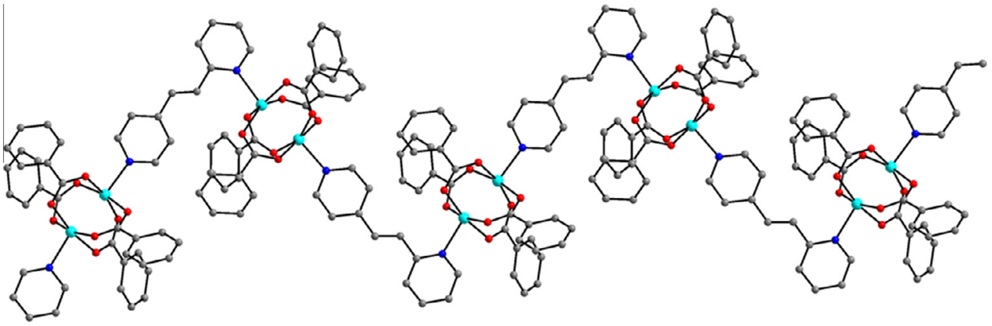


Fig. 1. One-dimensional structure of **1** containing paddle-wheel-type Cu_2 units. All hydrogen atoms and THF solvent molecules were omitted for clarity.

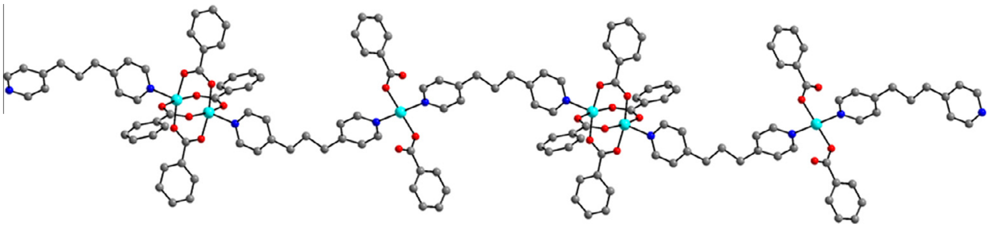


Fig. 2. One-dimensional structure of **2** containing alternating units of $[Cu_2(O_2CPh)_4]$ and $[Cu(O_2CPh)_2]$ connected by bpp. All hydrogen atoms were omitted for clarity.

benzoate-bridged 1-D Mn_6 compound. Unlike Zn–benzoate and Mn–benzoate systems, Cu–benzoate system afforded predominantly 1-D coordination polymers with a paddle-wheel building block unit.

3.1. Catalytic transesterification reactions by compounds *1*–*5* and *7*

Although an enormous number of polymeric compounds containing Cu ions have been reported over the last decade, their

Table 2
Selected bond distances and angles for compounds **1**–**7**.

	1	**2**	**3**	**4**	**5**	**6**[a]	**7**[b]
Cu–O (Å)	1.963(2)–1.993(2)	1.941(3)–1.975(3)	1.926(5)–1.987(5)	1.944(4)–1.964(4)	1.952(3)–1.978(3)	1.947(4)–1.998(3)	1.947(7)–2.000(8)
Cu–N (Å)	2.191(3), 2.136(3)	2.153(3), 2.032(5)	2.135(6), 2.162(5)	2.217(4)	2.192(3)	2.150(4)	2.198(4), 2.161(5)
Cu. . .Cu (Å)	2.6269(6)	2.6566(9)	2.652(2), 2.6540(18)	2.6285(13)	2.6079(9)	2.6417(8)	2.640(2), 2.620(3)
N–Cu–O (°)	89.65(11)–103.32(10)	89.79(16)–97.56(13)	88.67(19)–103.94(19)	90.17(15)–101.34(15)	91.37(11)–99.49(11)	87.43(16)–102.80(15)	92.3(3)–99.8(3)

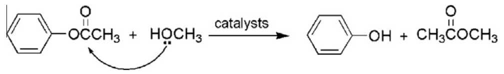
[a] See Ref. [18].
[b] See Ref. [52].

Table 3
Transesterification of esters with methanol in the presence of compounds **1**–**5** and **7** at 50 °C.[a]

Entry	Substrate	**1** (time/day)[b]	**2** (time/day)[b]	**3** (time/day)[b]	**4** (time/day)[b]	**5** (time/day)[b]	**7** (time/day)[b]
1	4-nitrophenyl acetate	0.38	0.16	0.29	0.33	0.38	0.38
2	4-fluorophenyl acetate	3	1	3	3	2	2
3	phenyl acetate	2	1	2	2	2	2
4	4-methylphenyl acetate	7	2	4	3	3	3
5	4-nitrophenyl benzoate[c]	2	0.5	2	2	2	2
6	4-chlorophenyl benzoate	6	2	4	6	4	4
7	phenyl benzoate	9	4	10	9	8	11
8	4-methylphenyl benzoate	10	5	10	9	12	12
9	vinyl acetate	0.29	0.14	0.25	0.21	0.21	0.33

[a] All esters were completely converted to the corresponding products, methyl acetate and methyl benzoate. Reaction conditions: esters, 0.05 mmol; catalyst, 1.15×10^{-3} mmol for **1**, 1.14×10^{-3} mmol for **2**, 1.23×10^{-3} mmol for **3**, 1.26×10^{-3} mmol for **4**, 1.16×10^{-3} mmol for **5** and 1.20×10^{-3} mmol for **7**; methanol (1 mL).
[b] Time necessary for the complete conversion of substrate to product.
[c] The solvent was a mixture of CH_3OH/CH_2Cl_2 (1/1) because of the low solubility of the substrate in methanol.

application as catalysts is relatively rare [11,56–60]. We have recently reported that the Cu-containing coordination polymer **6** formed from the reaction of $Cu(O_2CPh)_2$ with linear ligand 4,4′-bpy (4,4′-bipyridine) carried out the catalytic transesterification of a range of esters [18]. While this catalyst system constitutes a promising class of catalysts that appears to be an efficient, mild method for the alcoholysis of esters, there is still a high demand for the development of new types of highly efficient catalysts. To systematically study their catalytic reactivities in transesterification reactions, we explored the catalytic activity of new copper-containing polymers **1**–**5** and **7** using a wide range of esters with methanol [35,61]. The compounds **1**–**5** and **7** were found to perform the catalytic transesterification reaction efficiently. The treatment of phenyl acetate and methanol in the presence of the catalysts produced methyl acetate quantitatively under neutral conditions within 1–2 days (Eq. (1); see entry 3 of Table 3), while little transesterification occurred without the polymeric compounds. Interestingly, compound **2** is twice as efficient as the other compounds. To the best of our knowledge, the compound is the most efficient of the previously reported Cu-containing polymeric catalytic systems [56–58], and its efficiency is comparable to those of Zn-containing coordination and polymeric compounds that are well-known as efficient catalysts for these transesterification reactions [35,57,58,61]. More importantly, these results are surprising, because it has been reported that Cu-containing complexes or coordination polymers do not generally catalyze the transesterification reactions, whereas they has been known to be the good catalysts for epoxide ring-opening [18].



These promising results led us to further examine the transesterification of other esters, including *p*-substituted phenyl acetates and benzoates, by compounds **1**–**5** and **7**. The results are also given in Table 3. These compounds demonstrated high reactivity, completing the transesterification of *p*-nitrophenyl acetate, which contains an electron-withdrawing group, within 0.16–0.38 day (entry 1). 4-Fluorophenyl acetate and phenyl acetate displayed similar reactivities with the catalysts (entries 2 and 3). 4-Methylphenyl acetate showed somewhat decreased reactivity (entry 4). The transesterification of other esters by the catalysts was also performed efficiently (entries 5–9), although benzoates underwent slower transesterification than acetates. The *p*-nitrophenyl benzoate, with its electron-withdrawing substituent, underwent faster transesterification (entry 5), whereas the *p*-methylphenyl benzoate, with its electron-donating group, showed a slower reactivity (entry 8). Notably, vinyl acetate, which is widely used as a precursor for ester synthesis, was also converted efficiently to the product methyl acetate by the catalysts within 0.14–0.33 day (entry 9), suggesting that this catalytic system can be useful for preparing various esters by transesterification. This result suggests the possibility of using many of the Cu-containing polymeric compounds reported to date as potential catalysts for transesterification reactions.

It has been proposed that the mechanism of metal ion-catalyzed transesterification most likely involves electrophilic activation of the carbon center of the carbonyl moiety by binding of the metal to the carbonyl oxygen [35,50,51]. Therefore, the Lewis acidity of the metal center may be important in catalytic transesterification. Based on this idea, we used electrospray ionization mass spectrometry (ESI-MS) to detect the possible reactive species for the transesterification reaction in methanol. As shown in the ESI-Mass data (Figs. 3 and 4, and Figs. S11–S14), all compounds except for **2** might exist as paddle-wheel units in solution, while compound **2** may exist as a mononuclear type of Cu complex. These results are consistent with the X-ray structures of these compounds. Given these results, we propose a possible transesterification mechanism for these catalytic systems (Scheme 2). The substrate

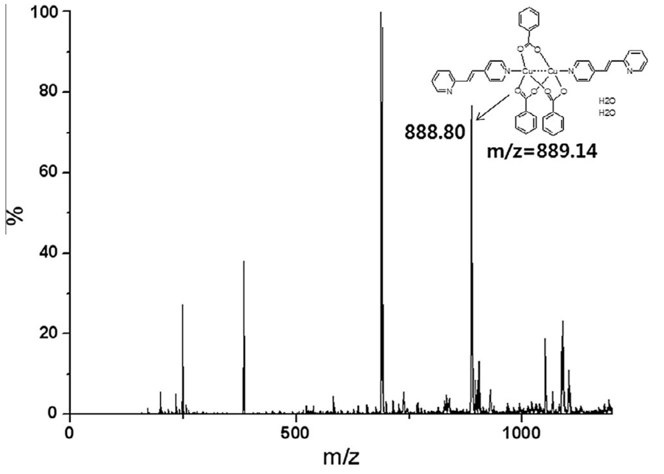


Fig. 3. Positive-ion electrospray ionization mass spectrum of complex **1** in MeOH.

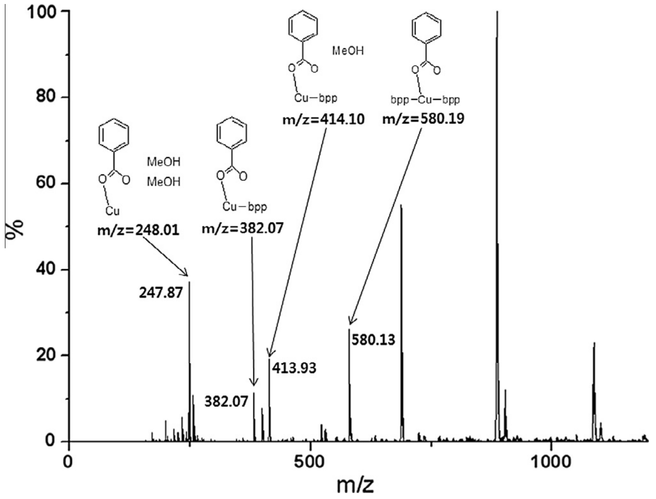
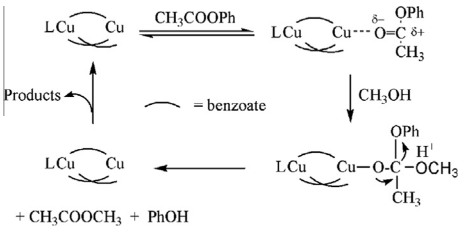


Fig. 4. Positive-ion electrospray ionization mass spectrum of complex **2** in MeOH.



Scheme 2. Proposed reaction mechanism for the transesterification reaction.

phenyl acetate binds to the Cu center of the paddle-wheel unit to give the adduct $(L)Cu_2(benzoate)_{2-4}(Sub)$. Then, the nucleophile methanol attacks the carbon atom of the carbonyl moiety of the adduct to produce the methyl acetate product. In the case of compound **2**, a mononuclear Cu complex might be a possible reactive species for the transesterification reaction, as interpreted from Fig. 4. Moreover, based on the proposed mechanism (Scheme 2) and the results of the transesterification reaction shown in Table 3, we could infer of why **2** with the mononuclear Cu complex unit shows the efficient transesterification reaction than **1**, **3**–**5**, and **7** with the dinuclear paddle-wheel complex units. As shown in Scheme 2, the substrate phenyl acetate could bind only to one side of the Cu paddle-wheel complex because the other side has no room for the substrate. In contrast, the mononuclear Cu complex of **2** can bind to the substrate in all directions (Scheme 1). Therefore, the steric effect of compound **1**, **3**–**5**, and **7** might slow down the transesterification reaction.

4. Conclusions

The paddle-wheel dinuclear unit consists of two Cu^{II} ions bridged by four benzoate ligands, and these paddle-wheel $[Cu_2(O_2CPh)_4]$ units are connected via various bridging ligands to form one-dimensional chained compounds formulated as $[Cu_2(O_2CPh)_4(\mu\text{-}L)]$ (L = 2,4-bpe (**1**), 3,3′-dipicam (**3**), 2,5-Me_2pyz (**4**), pyz (**5**), 4,4′-bpy (**6**), and 4-pds (**7**)). Compound **2**, formulated as $[[Cu_2(O_2CPh)_4][Cu(O_2CPh)_2](\mu\text{-}bpp)_2]$, consists of alternating units of $[Cu_2(O_2CPh)_4]$ and $[Cu(O_2CPh)_2]$ connected by bpp. Reactions of Cu-benzoate with various bipyridyl ligands predominantly produce 1-D coordination polymers containing paddle-wheel units, whereas Zn–benzoate and Mn–benzoate units afforded various structures depending on the bridging ligands. We have also shown that compounds **1–5** and **7** catalyzed the transesterification of a variety of esters. Notably, the transesterification by catalyst **2** with a mononuclear unit is very efficient and is the most efficient of the previously reported Cu-containing polymeric compounds. A mononuclear type of Cu complex might be the major reactive species for the transesterification reaction by compound **2**, whereas a possible reactive species of the other complexes might be a paddle-wheel unit in solution. Therefore, it has been proposed that the paddle-wheel dinuclear unit has a steric hindrance, resulting in a slow transesterification reaction. This result also suggests the possibility of using many of the Cu-containing polymeric compounds reported to date as potential catalysts for transesterification reactions.

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Appendix A. Supplementary material

CCDC 858917–858921 contain the supplementary crystallographic data for compounds **1**–**5**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ica.2013.03.043.

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