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Substituent effects of pyrazine on construction of crystal structures of Zn(II)-benzoate complexes and their catalytic activities (dinuclear, trinuclear, and pentanuclear to 1-D and 2-D)

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ABSTRACT

Several substituted pyrazine ligands (2,3-dimethylpyrazine, 2,6-dimethylpyrazine, 2,5-dimethylpyrazine, quinoxaline) as well as simple pyrazine have been employed to investigate how the bridging pyrazine ligand influences on construction of Zn-benzoate complexes. Simple pyrazine and 2,5-dimethlpyrazine are used as bridging ligands to form two-dimensional and one-dimensional polymeric compounds, respectively. The other quinoxaline and two dimethyl-substituted pyrazine ligands are used only as terminal ligands to form dinuclear, trinuclear, and pentanuclear complexes. This result indicates that the substituents of pyrazine are very important roles for construction of Zn-benzoate complexes. Interestingly, the compounds **1**–**5** catalyzed efficiently the transesterification of a variety of esters, and among them, the pentanuclear complex **3** showed the most efficient reactivity. The substrates with the electron-withdrawing substituents have undergone faster transesterification, while those with the electron-donating ones have shown slow reaction. In addition, *p*-nitrophenyl acetate and *p*-nitrophenyl benzoate, known to be problematic substrates for the transesterification reaction, were also converted quantitatively to the corresponding products. Selectivity test of primary over secondary alcohol protection in the presence of **3** has provided, exclusively, the primary acetate, propyl acetate, suggesting that this catalytic system can be potentially useful in selecting for primary alcohols.

1. Introduction

Coordination polymers through self-assembly have attracted considerable attention in recent years, not only due to their structural and topological novelty [1,2], but also for their potential applications as functional materials such as ion exchange [3], gas storage [4], molecular sensing [5], and catalysis [6]. While the control of structure and topology of assemblies is one of the major goals in coordination polymer chemistry, many efforts have been devoted to rational design of specific coordination polymers including one-, two-, and three-dimensional structures. Importantly, the structure of coordination polymers is highly influenced by many factors such as the coordination geometry of metal ions [7], the structure of organic ligands [8], the solvent system [9], pH value [10], temperature [11], the counteranion [12], and the ratio of ligands to metal ions [13]. In some cases, a subtle change in any of these factors can lead to new complexes with different structural topologies and different functions. So far, however, there is still little understanding concerning the factors that determine their synthesis and the resulting structure, and the attainment of rational control to give rise to desired topologies and specific properties still remains a great challenge.

Carboxylates constitute an important class of ligands in the formation of coordination polymers [14]. These ligands are capable of binding a metal in either a monodentate, bidentate or bridging mode that produce both mono- and polynuclear molecular and polymeric structures [15]. Moreover, zinc-carboxylate complexes are of interest for their relevance to biological systems [16] and have recently been employed as components in porous metal–organic framework materials [17]. In addition to mononuclear species [18], dinuclear [19], trinuclear [19], tetranuclear [20], heptanuclear [21] and compounds of higher nuclearity [22] have been reported. These types of polynuclear units can be used as building blocks to form polymeric compounds.

There are a few reports that simple substitutions on ligands can have profound effects on coordination geometry [8,23]. However, such an effect is seldom systematically considered in the assembly of zinc-carboxylate containing coordination polymers. Therefore, a systematic investigation for the understanding of the relationships between the structures of the coordination polymers and the nature

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of ligands, as well as other factors, is still important and necessary to be studied.

In order to prepare functional supramolecular complexes with intriguing structures and potential applications especially in catalysis and to systematically investigate the substituent effect of an organic ligand on the structure of zinc-carboxylate containing coordination polymers, in this work, we have reacted Zn-benzoate with pyrazine (pyz) and its derivatives, 2,3-dimethylpyrazine (2,3-Me_2pyz), 2,5-dimethylpyrazine (2,5-Me_2pyz), 2,6-dimethylpyrazine (2,6-Me_2pyz), and quinoxaline, and report herein five new Zn(II)-benzoate coordination architectures, **1** ($Zn_2(O_2CPh)_4$(quinoxaline)$_2$), **2** ($Zn_3(O_2CPh)_6$(2,3-Me_2pyz)$_2$), **3** ($Zn_5(\mu_3\text{-}OH)_2(O_2CPh)_8$(2,6-$Me_2$pyz)$_2$), **4** (1-D, $[Zn_2(O_2CPh)_4(2,5\text{-}Me_2pyz)]_n$), **5** (2-D, $[Zn(O_2CPh)(\mu_2\text{-}O_2CPh)(\mu_2\text{-}pyz)_{0.5}]_n$). Assembly of zinc(II)-benzoate with different types of pyrazine shows different structures, from dinuclear, trinuclear and pentanuclear complexes to one-dimensional and two-dimensional coordination polymers. Moreover, compounds **1**–**5** catalyzed efficiently the transesterification of a variety of esters.

2. Experimental

2.1. Materials

Acetone, methanol, ethanol, propanol, 2-propanol, *para*-substituted phenyl acetate, *para*-substituted phenyl benzoate, methylacetate, methylbenzoate, quinoxaline, 2,3-dimethylpyrazine, 2,6-dimethylpyrazine, 2,5-dimethylpyrazine, pyrazine, ammonium benzoate, and zinc nitrate 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 carried out by using an EA1108 (Carlo Erba Instrument, Italy) in the Organic Chemistry Research Center of Sogang University, Korea. IR spectra were measured on a BIO RAD FTS 135 spectrometer as KBr pellets. Product analysis for the transesterification reaction was performed on either a Hewlett–Packard 5890 II Plus gas chromatograph interfaced with Hewlett–Packard Model 5989B mass spectrometer or a Donam Systems 6200 gas chromatograph equipped with a FID detector using 30-m capillary column (Hewlett–Packard, HP-1, HP-5, and Ultra 2).

2.3. Synthesis of dinuclear zinc-benzoate with quinoxaline ligand ($Zn_2(O_2CPh)_4$(quinoxaline)$_2$) (1)

Thirty-eight milligrams (0.125 mmol) of $Zn(NO_3)_2 \cdot 6H_2O$ and 36.0 mg (0.25 mmol) of $C_6H_5COONH_4$ were dissolved in 4 mL water and carefully layered by 4 mL methanol solution of quinoxaline ligand (29.0 μL, 0.25 mmol). The yield was 55.0 mg (50.5%) for compound **1**. Suitable crystals of compound **1** for X-ray analysis were obtained in a month. *Anal.* Calc. for $C_{44}H_{32}N_4O_8Zn_2$ (875.48), **1**: C, 60.36; H, 3.69; N, 6.40. Found: C, 60.01; H, 3.62; N, 6.70%. IR (KBr): $\nu(\text{cm}^{-1})$ = 3434(br), 3068(w), 2369(m), 1641(s), 1574(w), 1505(w), 1402(s), 1068(w), 1039(w), 967(w), 866(w), 840(w), 764(m), 717(s), 680(m), 464(m).

2.4. Synthesis of trinuclear zinc-benzoate with 2,3-dimethylpyrazine ligand ($Zn_3(O_2CPh)_6$(2,3-Me_2pyz)$_2$) (2)

Thirty-eight milligrams (0.125 mmol) of $Zn(NO_3)_2 \cdot 6H_2O$ and 36.0 mg (0.25 mmol) of $C_6H_5COONH_4$ were dissolved in 4 mL water and carefully layered by 4 mL acetone solution of 2,3-dimethylpyrazine ligand (27.0 μL, 0.25 mmol). The yield was 60.0 mg (42.2%) for compound **2**. Slow evaporation of the diffused mixture provided suitable crystals of **2** for X-ray crystallography in a month. *Anal.* Calc. for $C_{54}H_{46}N_4O_{12}Zn_3$ (1139.06), **2**: C, 56.94; H, 4.08; N, 4.92. Found: C, 56.54; H, 4.10; N, 4.73%. IR (KBr): $\nu(\text{cm}^{-1})$ = 3061(s), 3030(w), 1973(w), 1919(w), 1829(w), 1638(br s), 1572(br s), 1421(br s), 1258(w), 1178(s), 1071(s), 1024(s), 978(m), 942(m), 884(w), 862(s), 841(s), 819(m), 723(s), 680(s), 596(w), 466(s), 438(m).

2.5. Synthesis of pentanuclear zinc-benzoate with 2,6-dimethylpyrazine ligand ($Zn_5(\mu_3\text{-}OH)_2(O_2CPh)_8$(2,6-$Me_2$pyz)$_2$) (3)

Thirty-eight milligrams (0.125 mmol) of $Zn(NO_3)_2 \cdot 6H_2O$ and 36.0 mg (0.25 mmol) of $C_6H_5COONH_4$ were dissolved in 4 mL methanol and carefully layered by 4 mL acetone solution of 2,6-dimethylpyrazine ligand (28.0 mg, 0.25 mmol). The yield was 32.0 mg (16.6%) for compound **3**. Slow evaporation of the diffused mixture provided suitable crystals of **3** for X-ray crystallography in a month. *Anal.* Calc. for $C_{68}H_{58}N_4O_{18}Zn_5$ (1546.03), **3**: C, 52.82; H, 3.79; N, 3.62. Found: C, 52.55; H, 4.00; N, 3.88%. IR (KBr): $\nu(\text{cm}^{-1})$ = 3440(br), 3066(m), 1603(s), 1565(s), 1416(br s), 1309(w), 1259(w), 1174(m), 1070(m), 1025(m), 942(w), 842(m), 719(s), 685(s), 576(w), 472(s).

2.6. Synthesis of one-dimensional polymeric compound containing zinc-benzoate with 2,5-dimethylpyrazine ligand (1-D, $[Zn_2(O_2CPh)_4(2,5\text{-}Me_2pyz)]_n$) (4)

Thirty-eight milligrams (0.125 mmol) of $Zn(NO_3)_2 \cdot 6H_2O$ and 36.0 mg (0.25 mmol) of $C_6H_5COONH_4$ were dissolved in 4 mL methanol and carefully layered by 4 mL acetone solution of 2,5-dimethylpyrazine ligand (27.0 μL, 0.25 mmol). The yield was 75.0 mg (72.8%) for compound **4**. Slow evaporation of the diffused mixture provided suitable crystals of **4** for X-ray crystallography in a month. *Anal.* Calc. for $C_{40}H_{36}N_4O_8Zn_2$ (831.47), **4**: C, 57.78; H, 4.37; N, 6.74. Found: C, 58.02; H, 4.11; N, 6.35%. IR (KBr): $\nu(\text{cm}^{-1})$ = 3741(w), 3431(br w), 3064(w), 2360(w), 1637(s), 1573(w), 1499(w), 1406(s), 1171(w), 1082(w), 1049(w), 1027(w), 840(w), 727(s), 715(s), 680(m), 464(w), 429(w).

2.7. Synthesis of two-dimensional polymeric compound containing zinc-benzoate with simple pyrazine ligand (2-D, $[Zn(O_2CPh)(\mu_2\text{-}O_2CPh)(\mu_2\text{-}pyz)_{0.5}]_n$) (5)

Thirty-eight milligrams (0.125 mmol) of $Zn(NO_3)_2 \cdot 6H_2O$ and 36.0 mg (0.25 mmol) of $C_6H_5COONH_4$ were dissolved in 4 mL water and carefully layered by 4 mL methanol solution of pyrazine ligand (20.0 mg, 0.25 mmol). The yield was 43.0 mg (24.7%) for compound **5**. Slow evaporation of the diffused mixture provided suitable crystals of **5** for X-ray crystallography in a month. *Anal.* Calc. for $C_{64}H_{48}N_4O_{16}Zn_4$ (1390.54), **5**: C, 55.28; H, 3.49; N, 4.03. Found: C, 54.96; H, 3.40; N, 3.98%. IR (KBr): $\nu(\text{cm}^{-1})$ = 3127(w), 3070(w), 1598(s), 1555(s), 1428(s), 1398(m), 1157(w), 1121(m), 1067(s), 1024(w), 859(w), 828(m), 715(s), 688(s), 558(w), 461(s), 424(m).

2.8. Catalytic activity of compounds 1–5

Catalytic homogeneous reaction conditions: Ester (0.05 mmol) was dissolved in an appropriate solvent (1 mL), methanol or propanol, and the catalyst (1.0 mg, 1.14×10^{-3} mmol for **1**, 1.0 mg, 0.88×10^{-3} mmol for **2**, 1.0 mg, 0.65×10^{-3} mmol for **3**, 1.0 mg, 1.20×10^{-3} mmol for **4**, and 1.0 mg, 0.72×10^{-3} mmol for **5**, respectively) was added and shaken in an incubator at 50 °C (450 rpm). Reaction conversion was monitored by GC/Mass analysis of 20 μL aliquots withdrawn periodically from the reaction mixture. All reactions were run at least three times and the average conversion yields are presented. We had the same results under N_2 instead of air, suggesting that air does not effect the transesterification reaction.

2.9. X-ray crystallography

The X-ray diffraction data for all five compounds were collected on a Bruker SMART APX diffractometer equipped with a monochromator in the Mo Kα (λ = 0.71073 Å) incident beam. Each 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 [24]. All hydrogen atoms were placed in the calculated positions. The crystallographic data for compounds **1**–**5** are listed in Table 1.

3. Results and discussion

3.1. Synthesis and spectral characterization

To investigate the effect of structure and substituent of organic ligands on the structure of their metal complexes, four pyrazine derivative ligands, quinoxaline, 2,3-dimethylpyrazine, 2,6-dimethylpyrazine, 2,5-dimethylpyrazine and simple pyrazine, were used to react with Zn(II)-benzoate. The coordination complexes **1**–**5** were prepared cleanly as single phase crystalline products and shows dinuclear **1**, trinuclear **2**, pentanuclear complexes **3**, one- **4** and two-dimensional **5** polymeric compounds, respectively. All five compounds are shown in Scheme 1. The infrared spectra of **1**–**5** were fully consistent with their formulations [25]. Sharp medium intensity bands in the range of ~1300 cm^{-1} to ~700 cm^{-1} were ascribed to stretching modes of the pyrazine ring moiety. Asymmetric and symmetric C═O stretching modes of the ligated benzoate moieties were evidenced by very strong, slightly broadened bands at ~1600 cm^{-1} and ~1400 cm^{-1}. The absence of any bands in the area of ~1710 cm^{-1} indicates full deprotonation of all carboxylate groups in **1**–**5**.

3.2. Dinuclear zinc-benzoate with quinoxaline ligand ($Zn_2(O_2CPh)_4(quinoxaline)_2$) (**1**)

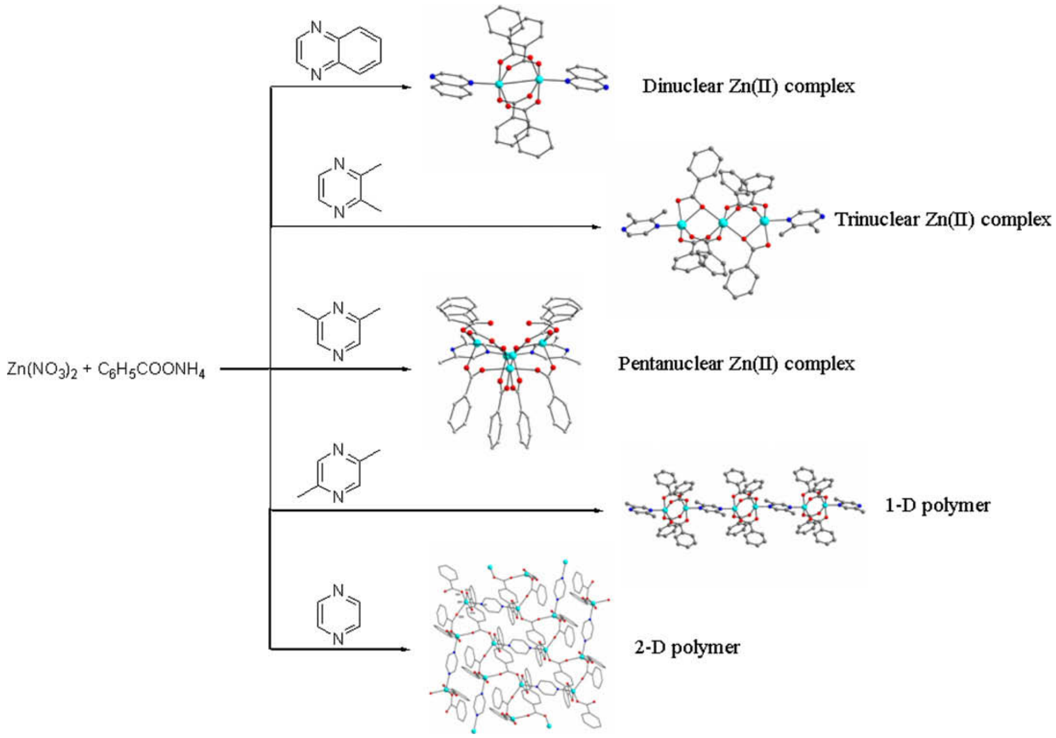
Asymmetric unit contains half of whole molecule, and there is an inversion center in the middle of Zn–Zn bond. Symmetric operation ($-x+2$, $-y+1$, $-z+1$) produces a paddle-wheel type dinuclear zinc-benzoate complex **1** (Fig. 1). The paddle-wheel type dinuclear complex is constructed by four bridging benzoate groups and two terminal quinoxaline ligands. Thus each Zn atom is NO4 donor penta-coordinated to form square pyramidal geometry. The similar paddle-wheel type of structures from zinc-benzoate or zinc-acetate have been reported in literature [19,26]. Zn–O bond distances range from 2.0191(15) to 2.0537(17) Å, Zn–N bond distance is 2.0792(18) Å which is typical in Zn(II) complexes, and Zn–Zn distance is 2.9900(7) Å (Table 2).

3.3. Trinuclear zinc-benzoate with 2,3-dimethylpyrazine ligand ($Zn_3(O_2CPh)_6(2,3\text{-}Me_2pyz)_2$) (**2**)

Asymmetric unit contains half of whole molecule, and there is a crystallographic inversion center on the central Zn atom. Symmetric operation ($-x+2$, $-y+2$, $-z+1$) produces a trinuclear zinc-benzoate complex **2** constructed by six bridging benzoate ligands and two axial 2,3-dimethylpyrazine ligands (Fig. 2) which is similar to the previously described trinuclear zinc-benzoate with axial pyridine ligands [19b]. Out of three Zn centers the central Zn is all O-donor hexa-coordinated from six benzoate groups to form a distorted octahedral geometry. The other two Zn centers are symmetric to each other, and each has a terminal 2,3-dimethylpyrazine ligand and four oxygen atoms from benzoate ligands. Thus each Zn2 center has NO4 coordination environment with a distorted trigonal bipyramid geometry. The coordination modes of benzoate ligands show two kinds of bridging modes [15]: one mode is a typical bridging mode, and the other is the unusual coordination mode that chelates to one Zn2 atom and, at the same time, bridges the other Zn1 atom as shown in Fig. 2. This unusual coordination mode of carboxylate group provides a big distortion around Zn2. In the typical bridging carboxylate coordination mode, Zn1–$O_{bridging}$ distances are 2.0362(15) and 2.0894(16) Å, and Zn2–$O_{bridging}$

Table 1
Crystallogrphic data for compounds **1**, **2**, **3**, **4**, and **5**

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{44}H_{32}N_4O_8Zn_2$	$C_{54}H_{46}N_4O_{12}Zn_3$	$C_{68}H_{58}N_4O_{18}Zn_5$	$C_{40}H_{36}N_4O_8Zn_2$	$C_{64}H_{48}N_4O_{16}Zn_4$
Formula weight	875.48	1139.06	1546.03	831.47	1390.54
Temperature (K)	293(2)	170(2)	170(2)	170(2)	170(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Space group	$P\bar{1}$	$P\bar{1}$	$P2/c$	$P\bar{1}$	$P2_1/c$
a (Å)	10.146(3)	10.7629(13)	11.644(12)	9.868(3)	14.197(3)
b (Å)	10.338(3)	11.3112(13)	11.639(13)	10.012(3)	6.2166(12)
c (Å)	10.444(3)	11.7684(14)	23.67(3)	11.865(3)	16.306(3)
α (°)	65.677(4)	61.846(2)	90.000	65.386(4)	90.000
β (°)	72.974(4)	78.843(2)	95.231(19)	89.490(5)	95.557(3)
γ (°)	81.781(4)	80.246(2)	90.000	63.081(4)	90.000
Volume (Å^3)	954.2(4)	1234.3(3)	3194(6)	926.6(4)	1432.4(5)
Z	1	1	2	1	1
D_{calc} (Mg/m^3)	1.524	1.532	1.607	1.490	1.612
Absorption coefficient (mm^{-1})	1.319	1.515	1.927	1.353	1.732
Crystal size (mm)	0.20 × 0.08 × 0.08	0.05 × 0.05 × 0.05	0.10 × 0.05 × 0.05	0.25 × 0.10 × 0.03	0.25 × 0.10 × 0.08
Reflections collected	5351	6947	17173	5202	7587
Independent reflections (R_{int})	3659 (0.0162)	4737 (0.0163)	6264 (0.0512)	3539 (0.0282)	2818 (0.0289)
Data/restraints/parameters	3659/0/262	4737/0/333	6264/0/435	3539/0/246	2818/0/199
Goodness-of-fit on F^2	1.099	1.037	1.056	0.946	1.059
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0315, wR_2 = 0.0827	R_1 = 0.0306, wR_2 = 0.0784	R_1 = 0.0391, wR_2 = 0.1007	R_1 = 0.0439, wR_2 = 0.0921	R_1 = 0.0327, wR_2 = 0.0815
R indices (all data)	R_1 = 0.0378, wR_2 = 0.0848	R_1 = 0.0392, wR_2 = 0.0811	R_1 = 0.0584, wR_2 = 0.1117	R_1 = 0.0631, wR_2 = 0.0966	R_1 = 0.0421, wR_2 = 0.0841
Largest difference in peak and hole (e Å^{-3})	0.226 and −0.371	0.317 and −0.513	0.550 and −0.418	0.598 and −0.300	0.487 and −0.260



Scheme 1.

distances are 1.9532(16) and 1.9453(16) Å. In the unusual coordination mode, Zn1–$O_{bridging}$ distance is 2.1744(16) Å which is a little longer than typical one, and Zn2–$O_{chelating}$ distances are 2.1804(17) and 2.1798(18) Å. Zn–N bond distance is 2.075(2) Å which is typical in Zn complexes. The Zn–Zn distance is 3.362(4) Å which is much longer than that of dinuclear one (Table 2).

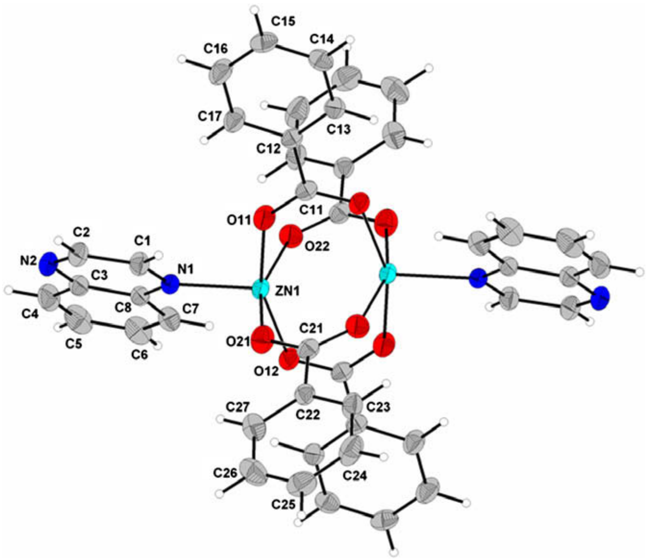


Fig. 1. Structure of dinuclear Zn complex **1**. Displacement ellipsoids are shown at the 30% probability level.

*3.4. Pentanuclear zinc-benzoate with 2,6-dimethylpyrazine ligand ($Zn_5(\mu_3\text{-}OH)_2(O_2CPh)_8(2,6\text{-}Me_2pyz)_2$) (**3**)*

Asymmetric unit contains half of whole molecule, and there is a C_2 axis through the middle Zn atom. Symmetric operation ($-x + 1$, y, $-z + 1/2$) produces a pentanuclear zinc-benzoate complex **3** constructed by six bridging benzoate ligands, two μ_3-hydoxyl ligands, two terminal 2,6-dimethylpyrazine ligands, and two terminal monodentate dangling benzoate ligands (Fig. 3). The central Zn1 ion is all O-donor hexa-coordinated from four benzoate ligands and two hydroxyl ligands to form a distorted octahedral geometry, and another two Zn2 ions are all O-donor tetra-coordinated from two bridging benzoate ligands, a dangling (monodentate)-benzoate ligand and a hydroxyl ligand to form a distorted tetrahedral geometry, and another two Zn3 ions are NO3-donor tetra-coordinated from two bridging benzoate ligands, a hydroxyl ligand and a 2,6-dimethylpyrazine ligand to form a distorted tetrahedral geometry. Importantly, this Zn-containing pentanuclear complex is unprecedented, to our best knowledge. The coordination modes of benzoate ligands are two types, bridging and monodentate (dangling) modes as shown in Fig. 3. A hydroxyl ligand bridges three Zn atoms. Zn–$O_{benzoate}$ bond distances range from 1.933(3) to

Table 2
Selected bond distances for compounds **1**, **2**, **3**, **4**, and **5**

	1	2	3	4	5
Zn–O (Å)	2.0191(15)– 2.0537(17)	1.9454(16)– 2.1804(17)	Zn–O(benzoate) 1.933(3)– 2.083(3) Zn–O(hydroxyl) 1.941(3)–2.111(3)	2.017(2)– 2.063(2)	Zn–O(bridging benzoate) 1.9627(17), 1.9924(17) Zn–O(chelating benzoate) 2.0068(18), 2.3407(18)
Zn–N (Å)	2.0792(18)	2.075(2)	2.013(3)	2.083(2)	2.085(2)
Zn–Zn (Å)	2.9900(7)	3.362(4)	3.143(2)–3.397(4)	2.9525(10)	N/A

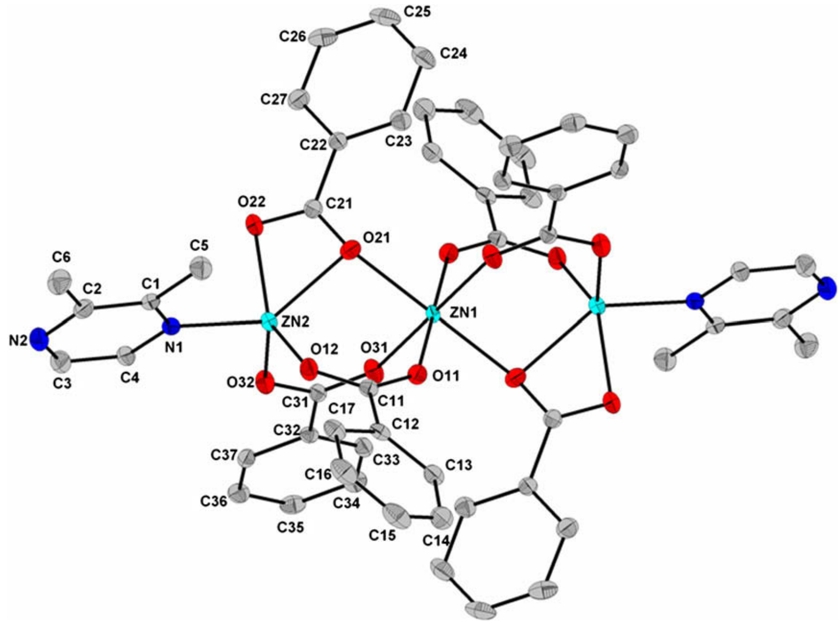


Fig. 2. Structure of trinuclear Zn complex **2**. Displacement ellipsoids are shown at the 30% probability level.

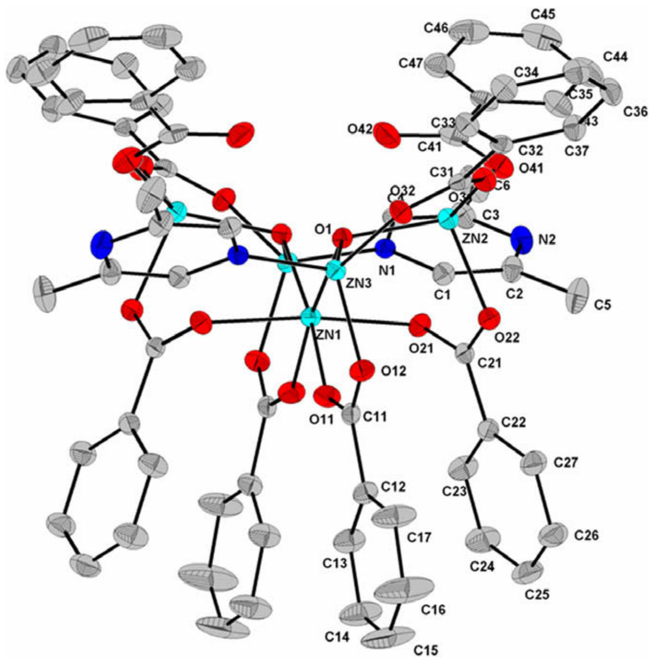


Fig. 3. Structure of pentanuclear Zn complex **3**. Displacement ellipsoids are shown at the 30% probability level. All hydrogen atoms were omitted for clarity.

2.083(3) Å, Zn–$O_{hydroxyl}$ bond distances range from 1.941(3) to 2.111(3) Å, and Zn–N bond distance is 2.013(3) Å which is typical in Zn complexes. The Zn1–Zn2, Zn1–Zn3, and Zn2–Zn3 distances are 3.295(21), 3.397(4), 3.143(2) Å, respectively (Table 2).

*3.5. One-dimensional polymeric compound containing zinc-benzoate with 2,5-dimethylpyrazine ligand (1-D, $[Zn_2(O_2CPh)_4(2,5\text{-}Me_2pyz)]_n$) (**4**)*

The crystal structure of **4** is shown in Fig. 4. The paddle-wheel type units are bridged by 2,5-dimethylpyrazine to form a one-dimensional polymeric compound. The paddle-wheel type units are similar to those of compound **1**. Zn–O bond distances range from 2.017(2) to 2.063(2) Å, which are almost close to those in **1**, and Zn–N bond distance is 2.083(2) Å which is typical in Zn(II) complexes. Zn–Zn distance is 2.9525(10) Å (Table 2), that is shorter than that of the discrete dinuclear complex **1**. The Zn′–Zn–N bond angle (175.25(1)°) shows a nearly linear chain structure. Interestingly, this compound shows an one-dimensional structure unlike **1**, **2**, and **3**. The coordination mode of benzoate shows only bridging type as shown in Fig. 4. In case of similar one-dimensional compound $[Zn_2(bpy)(OAc)_4]_n$, acetate bridged dinuclear Zn_2 unit is not a paddle-wheel type, and each Zn(II) ion has different coordination geometry: Zn1 has an octahedral geometry and Zn2 has a trigonal bipyramid geometry [27].

*3.6. Two-dimensional polymeric compound containing zinc-benzoate with simple pyrazine ligand (2-D, $[Zn(O_2CPh)(\mu_2\text{-}O_2CPh)(\mu_2\text{-}pyz)_{0.5}]_n$) (**5**)*

Asymmetric unit contains a Zn atom, two benzoate ligands, and half pyrazine, and symmetry operations ($-x+2$, $-y+3$, $-z+2$), ($-x+2$, $y+1/2$, $-z+3/2$), and ($-x+2$, $y-1/2$, $-z+3/2$) produce a two-dimensional polymeric compound (Fig. 5). Mononuclear $Zn(O_2CPh)$ units are bridged by bridging benzoate and pyrazine ligands to form a two-dimensional sheet. Thus, the Zn atom has NO4-donor penta-coordinated environment. The coordination modes of benzoate ligands show two types, bridging and chelating modes as shown in Fig. 5. Zn–$O_{bridging}$ bond distances are 1.9627(17) and 1.9924(17) Å, and Zn–$O_{chelating}$ bond distances are 2.0068(18) and 2.3407(18) Å. Zn–N bond distance is 2.085(2) Å which is typical in Zn complexes (Table 2). Pyrazine does not have any substituents on its own ring, indicating no steric effect. Therefore, pyrazine may produce 2-D structure. However, in case of using acetate ligands instead of benzoate ligands, an unusual heptanuclear complex $Zn_7(\mu_4\text{-}O)_2(OAc)_{10}(pyz)_2$ has been made by reaction of $Zn(OAc)_2 \cdot 2H_2O$ with pyrazine (pyz) in refluxing ethanol [21]. The structure of the heptanuclear complex revealed a central Zn core in which two pseudo-tetrahedral Zn_4 units are joined at a common vertex, and two pyrazine molecules are bound as terminal ligands. Furthermore, $Cu_2(O_2CPh)_4$-pyz system showed a linear one-dimensional [28]. The structure of $Cu_2(O_2CPh)_4$-pyz showed the linear geometry with the chain skeleton bridged by pyrazine in axial direction of the paddle-wheel type Cu_2 core which is similar to our one-dimensional compound **4** containing

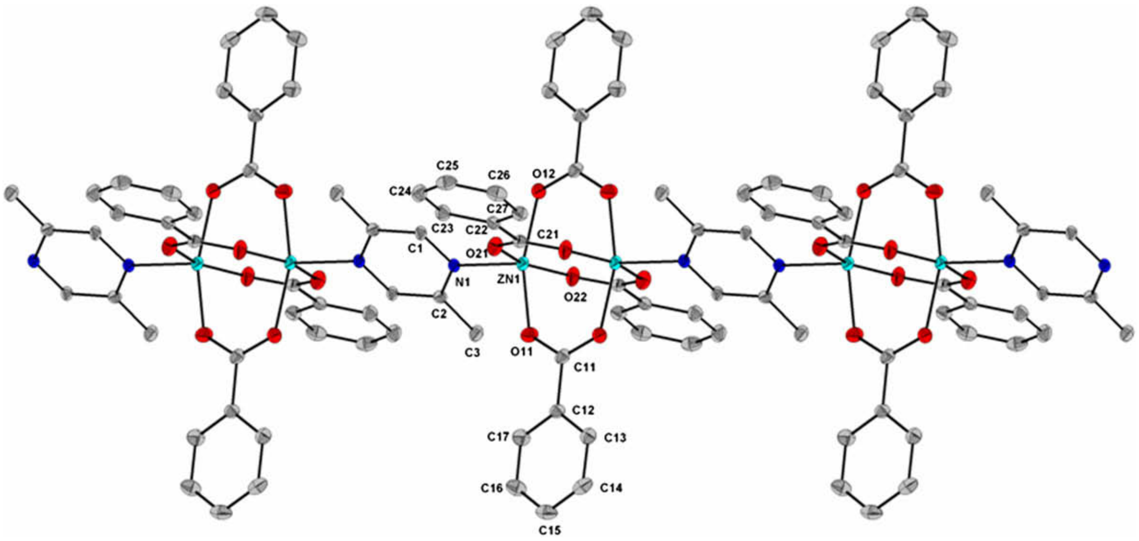


Fig. 4. Structure of one-dimensional Zn complex **4** containing paddle-type dinuclear Zn units. Displacement ellipsoids are shown at the 30% probability level. All hydrogen atoms were omitted for clarity.

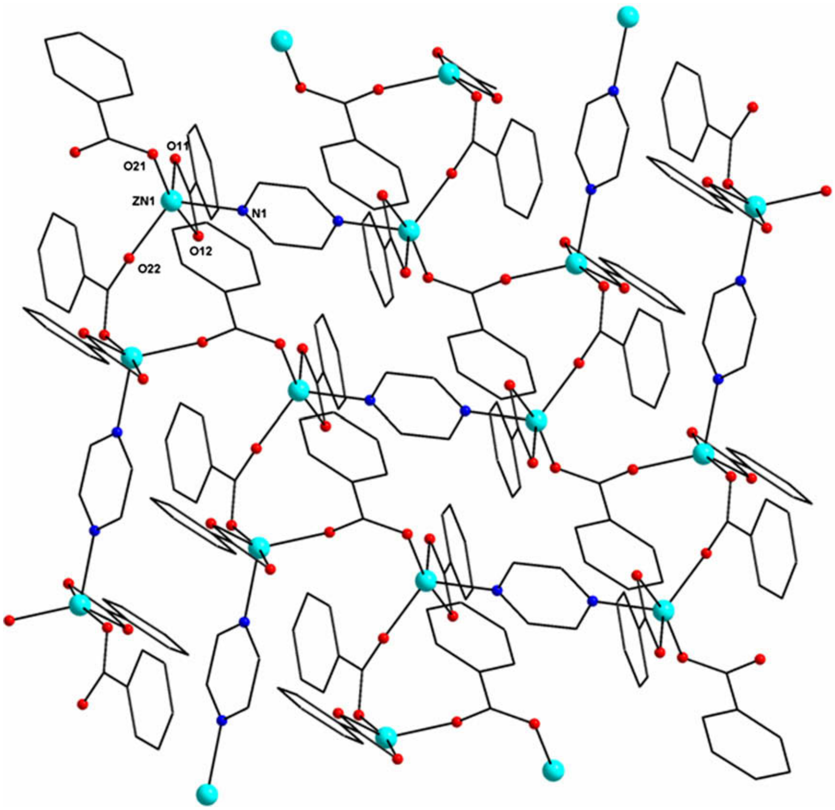


Fig. 5. Structure of two-dimensional Zn complex **5** containing Zn($O_2CC_6H_5$) units. All hydrogen atoms were omitted for clarity.

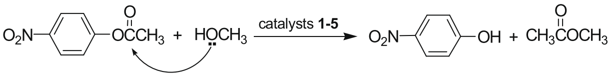
2,5-dimethylpyrazine. These different results might be because of (1) using different metal ions (Cu(II) versus Zn(II)), (2) using different ligands (acetate versus benzoate) and (3) using different reaction conditions from our self-assembly system.

3.7. Influence of the substituents of the organic ligand on the structure of the coordination compounds

To investigate how the change of the substituents of the bridging pyrazine ligand influences on construction of Zn-benzoate complexes, substituted pyrazine ligands (2,3-dimethylpyrazine, 2,6-dimethylpyrazine, 2,5-dimethylpyrazine, and quinoxaline) as well as simple pyrazine have been employed. Simple pyrazine and 2,5-dimethlpyrazine are used as bridging ligands to form two-dimensional and one-dimensional polymeric compounds, respectively. The other quinoxaline and two dimethyl-substituted pyrazine ligands are used only as terminal ligands to form dinuclear, trinuclear, and pentanuclear complexes. The structures of complexes **1**–**5** clearly show that the change of the substituents on the pyrazine ring are critical in the construction of molecular architecture of Zn-benzoate complexes. The coordination modes of benzoate ligand are also different according to the change of the substituents of pyrazine. Complexes **1** and **4** have only a bridging coordination mode, and **2** shows two different coordination modes, unusual chelating and bridging. **3** and **5** have two different coordination modes (bridging and monodentate (dangling) modes for **3** and bridging and chelating modes for **5**). These results suggest that selection of appropriate substituted groups would be an ideal way to construct novel metal-pyz coordination polymers.

*3.8. Catalytic transesterification reactions by the compounds **1**–**5***

Transesterifications are important transformations in organic synthesis in industrial as well as in academic laboratories [29]. Although there are many catalysts available for transesterification, they require harsh reaction conditions such as high reaction temperatures and acidic conditions [30]. Such drawback experienced with these catalysts derives us to develop new catalysts that operate under milder conditions. Therefore, as part of our efforts to design transesterification catalysts based on metal ions that are not redox active, we have recently reported that Zn-containing coordination polymers could carry out the catalytic transesterification of a range of esters with methanol at room temperature under the mild conditions [31]. While these catalyst systems constitute a promising class of catalysts that appears to be an efficient, mild, and easily recyclable method for the alcoholysis of esters, there is still more demand to develop new type of catalysts that show a high efficiency. Based on the previous results, therefore, compounds **1**–**5** have been also employed as a homogeneous catalyst for transesterification reaction in methanol. The ester, *p*-nitrophenyl acetate, was initially used as a substrate (Eq. (1)).



(1)

We observed that compounds **1**–**5** catalyzed the reaction of methanol with phenyl acetate, with quantitative conversion to methyl acetate in 0.04–0.5 day (1–12 h; see the entry 1 of Table 3) at 50 °C under the homogeneous neutral conditions. Among them, pentanuclear complex **3** shows the most efficient reactivity. Importantly, this result is best among the catalytic systems reported previously in Zn-containing coordination and polymeric compounds, to our best knowledge [31,32]. Once having established that **1**–**5** represent excellent catalysts for the transesterification reaction of *p*-nitrophenyl acetate with methanol, we have investigated the transesterification of various *p*-substituted phenyl acetates and benzoates. The substrates with the electron-withdrawing substituents have undergone faster transesterification (entries 1 and 5), while those with the electron-donating ones have shown slow reaction (entries 4 and 8). In addition, *p*-nitrophenyl acetate and *p*-nitrophenyl benzoate, known to be problematic substrates for the transesterification reaction due to undesirable side reactions such as isomerization or polymerization [33], were also converted quantitatively to the corresponding products.

Transesterification of esters with alcohol cannot, sometimes, achieve high conversions since the reaction is reversible. To solve this problem, therefore, enol esters are usually used as acylating agents, since the resultant enolate is converted to an aldehyde or ketone that is unable to participate in the reverse reaction [34]. In this work, vinyl acetate was used as an acylating agent and, expectedly, converted efficiently to the product methyl acetate within 0.06–0.5 day by **1**–**5** (entry 9), suggesting that this catalytic system can be useful for preparing various esters by transesterification.

Moreover, this promising result led us to test the transesterification with more challenging nucleophiles such as ethanol, 2-propanol, and propanol, in the presence of the most efficient catalyst **3**. Phenyl acetate reacted very slowly with either ethanol (70 days) or 2-propanol (75 days), respectively, whereas propanol drove the reaction to completion within 4 days (the sixth column in Table 3). Various esters were also examined with propanol as a nucleophile in the presence of **3**. The substrates with the electron-withdrawing substituents have undergone faster conversion to the corresponding products (entries 1 and 5 of the sixth column), while those with the electron-donating ones have shown slow transesterification reaction (entries 4 and 8 of the sixth column).

Table 3
Transesterification of esters by methanol and propanol in the presence of compounds **1**, **2**, **3**, **4**, and **5** at 50 °C[a]

Entry	Substrate	**1** (time/days)[b]	**2** (time/days)[b]	**3** (time/days)[b]		**4** (time/days)[b]	**5** (time/days)[b]
		MeOH[c]	MeOH[c]	MeOH[c]	PrOH[d]	MeOH[c]	MeOH[c]
1	4-Nitrophenyl acetate	0.21	0.5	0.04	1	0.25	0.13
2	4-Fluorophenyl acetate	4	1.5	1	4	3	2
3	Phenyl acetate	2	1.5	0.37	4	2	2
4	4-Methylphenyl acetate	9	4	1	8	6	6
5	4-Nitrophenyl benzoate[e]	3	0.5	0.21	13	3	3
6	4-Chlorophenyl benzoate	3	2	1	11	3	4
7	Phenyl benzoate	7	4	0.83	26	7	7
8	4-Methylphenyl benzoate	6	3	1	25	6	6
9	Vinyl acetate	0.46	0.5	0.06	3	0.35	0.42

[a] All esters were completely converted to the corresponding products, methyl acetate and methyl benzoate. Reaction conditions: esters; 0.05 mmol, catalyst; 1.14×10^{-3} mmol for **1**, 0.88×10^{-3} mmol for **2**, 0.65×10^{-3} mmol for **3**, 1.20×10^{-3} mmol for **4**, 0.72×10^{-3} mmol for **5**, solvent; methanol or propanol (1 mL). See Section 2 for the detailed reaction conditions.

[b] Time necessary for the complete conversion of substrate to product.

[c] Transesterification of esters was carried out in methanol (MeOH).

[d] Transesterification of esters was carried out in propanol (PrOH).

[e] The solvent was a mixture of MeOH/CH_2Cl_2 or PrOH/CH_2Cl_2 (1/1) because of low solubility of substrate in MeOH or PrOH.

Protection of a primary alcohol in the presence of a secondary alcohol is useful in natural product synthesis [34,35]. Therefore, selectivity of primary over secondary alcohol protection has been tested with the catalyst **3**. In a mixture of propanol and 2-propanol in the presence of **3** and phenyl acetate, only the propanol reacted, providing propyl acetate in 99.7% yield while the secondary acetate formed in <0.3% yield. This reaction clearly demonstrates the potential utility of our catalyst in selecting for primary alcohols.

Though we do not know, at this moment, about the exact reactive species and the reaction mechanism for the transesterification reaction by the catalysts, it has been proposed that the mechanism of metal ion catalyzed transesterification probably involves electrophilic activation of the carbon center of the carbonyl moiety by binding of the metal to the carbonyl oxygen [16]. Therefore, Lewis acidity of the metal center may be important in catalytic transesterification. Based on this idea, a possible transesterification mechanism in this catalyst system can be proposed. The substrate phenyl acetate substitutes a labile ligand, maybe benzoate, to give the adduct $-Zn-O{=}CR_1(OR_2)R$. Then, the nucleophile methanol would attack the carbon atom of carbonyl moiety of the adduct to produce the product methyl acetate. Detailed mechanistic studies are currently under investigation.

4. Conclusions

To investigate the influence of the substituent change of ligands on the crystal structure, five new coordination polymers constructed by self-assembly of the pyrazine and its derivatives and zinc(II)-benzoate have been structurally characterized. Simple pyrazine and 2,5-dimethlpyrazine are used as bridging ligands to form two-dimensional and one-dimensional polymeric compounds, respectively. The other quinoxaline and two dimethyl-substituted pyrazine ligands are used only as terminal ligands to form dinuclear, trinuclear, and pentanuclear complexes. The structural differences between such complexes reveal that the change of the substituents of the ligands has a great influence on the complex structures. This approach may be useful for synthesizing other complexes with high-dimensional structures. We have also shown that the compounds **1**–**5** catalyzed efficiently the transesterification of a variety of esters. Among them, pentanuclear complex **3** shows the most efficient reactivity. In addition, the scope of the application of **3** as a transesterification catalyst has been expanded to now include ethanol and propanol. Moreover, selectivity test of primary over secondary alcohol protection in the presence of **3** and phenyl acetate has provided, exclusively, the primary acetate propyl acetate, demonstrating the potential utility of our catalyst in selecting for primary alcohols. Furthermore, this observation is very significant since it encourages us to construct new polymeric compounds that might be efficiently used as heterogeneous catalysts friendly to the environment.

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Appendix A. Supplementary data

CCDC 661363, 661364, 661365, 661366 and 661367 contain the supplementary crystallographic data for **1**, **2**, **3**, **4** and **5**. These 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) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. X-ray powder diffraction patterns on the bulk samples for **1**–**5** are also available. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2008.08.010.

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