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Novel chains constructed from heterotrinuclear units and 1,2-bis(4-pyridyl)ethane formulated as $[M_2M'(O_2CPh)_6](bpa)$ (M = Co, Zn, M′ = Co, Cd): Their catalytic activity

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ABSTRACT

Three novel heterometallic complexes containing two bridging ligands bpa and benzoate, formulated as $[M_2M'(O_2CC_6H_5)]_n(bpa)_n$ (bpa = 1,2-bis(4-pyridyl)ethane, M_2M' = Zn_2Co (**1**), Zn_2Cd (**2**), and Co_2Cd (**3**)), have been synthesized. All three compounds show one-dimensional structures containing linear heteronuclear coordination units linked by bridging bpa ligands. Reactivity study of the compounds **1**–**3** for the transesterification of a variety of esters has shown that they are very efficient and **2** is the best among them.

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Coordination polymers through self-assembly have attracted considerable attention in recent years, not only due to their structural and topological novelty [1], but also for their potential applications as functional materials such as ion exchange, gas storage, molecular sensing, and catalysis [2]. Significantly, the structure of coordination polymers is highly influenced by many factors such as the coordination geometry of metal ions, the structure of organic ligands, the solvent system, pH value, temperature, the counteranion, and the ratio of ligands to metal ions [3]. In some cases, a subtle change in any of these factors can lead to new complexes with different structural topologies and different functions [3]. Among these factors, the incorporation of two or more transition heterometals in a coordination polymer is a current challenge for designed synthesis, since the incorporation of two heterometals can increase the diversity of the coordination polymers [4]. Therefore, heterometallic coordination polymers are now being increasingly investigated for opportunities to incorporate unusual metal coordination environments to enhance catalytic, photoluminescent, or other properties.

There are some reports that the incorporation of two or more transition heterometals into a coordination polymer can have profound effects on coordination geometry [4]. However, such an effect is seldom considered in the assembly of metal-benzoate-containing coordination polymers, except for only an example that redox-active ligands such as tetrathiafulvalene (TTF) derivatives have been applied to the heterometallic trinuclear complexes formulated as $Co^{II}_2M^{II}(PhCOO)_6(L)_2 \cdot 2CH_3CN$ (L = 4-[2-(tetrathiafulvalenyl)ethenyl]pyridine, M = Co^{II}, Mn^{II}) which show antiferromagnetic coupling leading to a magnetic ground state [5]. Therefore, a further investigation for the understanding of the relationships between the structures of the coordination polymers containing benzoate and the incorporation of two or more transition metals is important and necessary to be studied.

In our efforts to investigate the control of the self-assembly of functional supramolecular complexes with intriguing structures and potential applications in catalysis, we have recently carried out a systematic study of various metal–organic complexes from the mixed-ligand systems of multifunctional organic ligand benzoate and bridging ligands such as pyrazine, its derivatives, 4,4′-bipyridine, and 1,2-bis(4-pyridyl)ethane [6]. Importantly, the assembly process of metal benzoates and bipyridyl ligands has been, also, highly influenced by solvent system, pH, metal to ligand ratio, and the coordination geometry of metal ions [6].

As an extension of our previous work, in this study, we have investigated the complex formation of two heterometal ions with two bridging ligands bpa and benzoate in order to further prepare functional supramolecular complexes with intriguing structures and potential applications especially in catalysis.

We present, for the first time, three new heterometallic complexes containing two bridging ligands bpa and benzoate,

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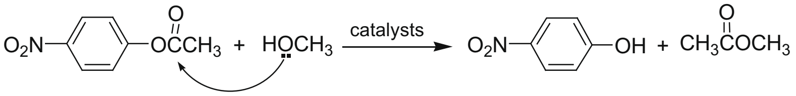
formulated as $[M_2M'(O_2CPh)_6]_n(bpa)_n$ (bpa = 1,2-bis(4-pyridyl)ethane, M_2M' = Zn_2Co (**1**), Zn_2Cd (**2**), and Co_2Cd (**3**)), which show the catalytic activities for transesterification reactions. They were prepared by a direct diffusion technique where an aqua solution of the mixture of $M(NO_3)_2$, $M'(NO_3)_2$ and ammonium benzoate is carefully layered by a polar solvent of bpa ligands [7].

The three compounds are isostructural [8], and a centrosymmetric trinuclear unit is shown in Fig. 1. The hetero-metal trinuclear units consist of three metal ions bridged by benzoate ligands, and they are connected by bpa ligands to form one-dimensional chains (Fig. 2). In the trinuclear unit, two benzoates coordinate to metal ions in a bridging mode (for O11–C11–O12 and O21–C21–O22 carboxylates) among four possible coordination modes [6] and the other one coordinates in chelating/bridging mode (for O31–C31–O32 carboxylate). The central hetero-metal ion [M′1] is lying on an inversion center, and its coordination geometry is distorted octahedral from six benzoate oxygen atoms. Central octahedron in **1** has six Co–O distances ranging from 2.0300(15) to 2.197(2) Å, and those in **2** and **3** have also six Cd–O distances (2.173(3)–2.333(3) Å for **2** and 2.194(7)–2.286(9) Å for **3**). The coordination geometry of outer metal [M1] ions is distorted trigonal bypyramodal from four oxygen atoms and one nitrogen atoms: three oxygen atoms from three different benzoates (Zn–O 1.9615(18)–2.1050(18) Å for **1**, Zn–O 1.966(3)–2.027(3) Å for **2**, and Co–O 2.077(8)–2.280(11) Å for **3**), one nitrogen atom from bpa (Zn–N 2.036(2) Å for **1**, Zn–N 2.032(3) Å for **2**, and Co–N 2.149(9) Å for **3**), and fifth oxygen atom from the chelating/bridging benzoate (Zn–O 2.269(2) Å for **1**, Zn–O 2.433(4) Å for **2**, and Co–O 2.356(12) Å for **3**). A similar coordination arrangement around the outer M ions was found in comparable $Co^{II}_2Mn^{II}(PhCOO)_6$ complex [5]. M···M′ distances for **1**, **2**, and **3** are 3.36(7) Å, 3.302(5) Å, and 3.459(8) Å, respectively. Besides **1**, **2**, and **3** systems, other heterometal combinations have been tested (for examples; Zn/Ni, Zn/Cu, Cd/Ni, Co/Ni, etc.), but only homometal-containing compounds formed. These results may be due to the coordination mode of metal ions.

We have recently shown a systematic investigation on the coordination polymers assembled from metal benzoates and bpa ligands [6]. They showed two kinds of structures: parallelogram-like two-dimensional sheets for Co, Ni, and Cd, and one-dimensional chains for Mn, Cu, and Zn. Importantly, the compounds containing non-redox metals (Zn and Cd) catalyzed efficiently the transesterification of a variety of esters. This result led us to attempt the transesterification reaction using the compounds **1**–**3**. Treatment of 4-nitrophenyl acetate and methanol in the presence of the catalysts **1**–**3** at 50 °C produced methyl acetate quantitatively under the homogeneous neutral conditions within 0.17–0.63 day (Eq. (1); see entry 1 of Table 1), respectively, while trace or a small amount of transesterification occurs without each catalyst [6].



(1)

Among them, the compound **2** showed the most efficient reactivity. Importantly, this result is the first example that the mixed-metal polymers containing benzoate catalyze the transesterification reactions, to our best knowledge [4]. In addition, this efficient reactivity is one of best among the catalytic systems reported previously in Zn- or Cd-containing coordination and polymeric compounds [2h,6]. Further, 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). Moreover, vinyl acetate, that is widely used as a precursor for ester synthesis [9], was also converted efficiently to the product methyl acetate by the catalysts **1**–**3** within 0.23–0.63 day (entry 9), suggesting that this catalytic system can be useful for preparing various esters by transesterification.

Though we do not know, at this moment, about the exact reactive species and the reaction mechanism for the transesterification reaction by the catalysts, we can propose the possible reactive species by a comparison of the present and previous results [6b]. In compound **1**, Zn-containing complex in solution might be the reactive species, because the reactivity of **1** is similar to that of the homometal polymer $[(Zn_3(O_2CPh)_6)(\mu\text{-bpa})(Zn_2(O_2CPh)_4)]_n$ previously obtained from the reaction of zinc benzoate and bpa [6b]. In the same way, both Zn and Cd complexes for **2** and Cd-containing complex for **3** might be the reactive species. These complexes may catalyze the transesterification reactions that probably involve electrophilic activation of the carbon center of the carbonyl moiety by binding of the metal to the carbonyl oxygen, based on

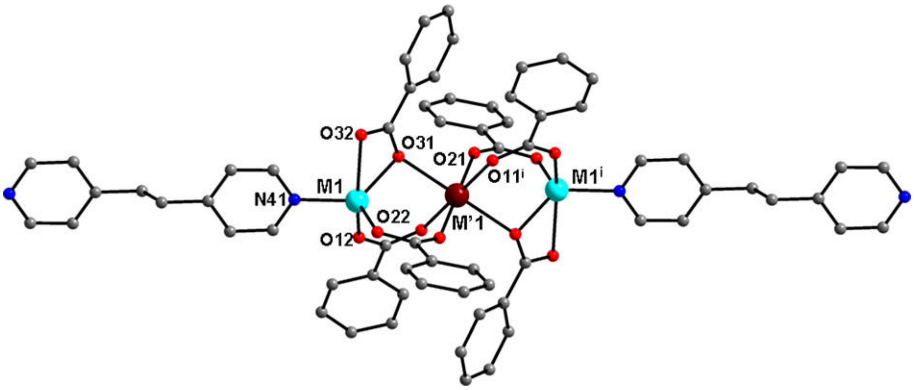


Fig. 1. A trinuclear unit in heterometallic complexes formulated as $[M_2M'(O_2CPh)_6]_n(bpa)_n$. Symmetry operation: i (1 − *x*, −*y*, 1 − *z*) for **1**, (2 − *x*, −*y*, 1 − *z*) for **2**, (2 − *x*, 2 − *y*, 1 − *z*) for **3**.

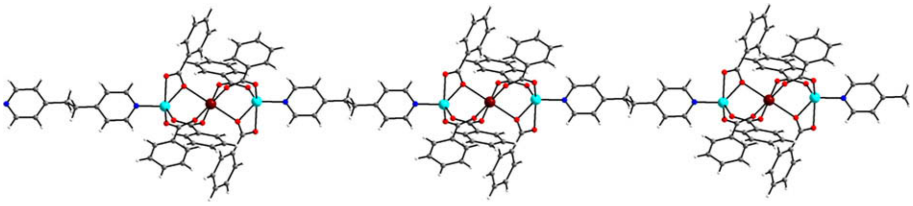


Fig. 2. One-dimensional structure containing trinuclear heterometallic units in **1**–**3**.

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

Entry	Substrate	**1** (time/days)[b]	**2** (time/days)[b]	**3** (time/days) [b]
1	4-Nitrophenyl acetate	0.17	0.25	0.63
2	4-Fluorophenyl acetate	8	7	31
3	Phenyl acetate	1.29	1	5
4	4-Methylphenyl acetate	1.29	1	7
5	4-Nitrophenyl benzoate [c]	1.67	1	13
6	4-Chlorophenyl benzoate	2	1.58	7
7	Phenyl benzoate	4	4	17
8	4-Methylphenyl benzoate	4	4	21
9	Vinyl acetate	0.23	0.25	0.63

[a] All esters were completely converted to the corresponding products, methyl acetate and methyl benzoate. *Reaction conditions*: esters; 0.05 mmol, catalyst; 1.0 mg, 0.88×10^{-3} mmol for **1**, 1.0 mg, 0.91×10^{-3} mmol for **2**, 1.0 mg, 0.87×10^{-3} mmol for **3**, solvent; methanol (1 mL). See Supplementary material for the detailed reaction conditions.

[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 low solubility of substrate in CH_3OH.

our previous results [6]. Detailed mechanistic studies are currently under investigation.

In summary, we have synthesized three novel heterometallic complexes containing two bridging ligands bpa and benzoate formulated as $[M_2M'(O_2CPh)_6]_n(bpa)_n$ ($M_2M' = Zn_2Co$ (**1**), Zn_2Cd (**2**), and Co_2Cd (**3**)). All three compounds show one-dimensional structures containing linear heteronuclear coordination units linked by bridging bpa ligands. These complexes could also carry out the catalytic transesterification of a range of esters with methanol at room temperature under the mild conditions. This observation is very significant since it encourages us to construct new polymeric compounds that might be efficiently used as catalysts for a variety of transformation reactions such as epoxide ring-opening, transesterification, epoxidation, and etc.

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Appendix A. Supplementary material

CCDC 744691, 744692 and 744693 contain the supplementary crystallographic data for this paper. 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 doi:10.1016/j.inoche.2009.10.028.

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[7] Preparation of **1**: 18.2 mg (0.06 mmol) of $Zn(NO_3)_2$ hexahydrate, 17.8 mg (0.06 mmol) of $Co(NO_3)_2$ hexahydrate and 34.0 mg (0.24 mmol) of ammonium benzoate were dissolved in 4 mL H_2O and carefully layered by 4 mL acetone solution of 1,2-bis(4-pyridyl)ethane ligand (22.3 mg, 0.12 mmol). Suitable crystals of compound **1** for X-ray analysis were obtained in a week. Compound **1** was stable below 345 °C from thermal gravimetric analysis (TGA). IR (KBr): $\nu(\mathrm{cm}^{-1}) = 3437$(brm), 3064(m), 2950(w), 1607(s), 1567(s), 1399(s), 1228(m), 1175(w), 1069(m), 1028(m), 939(w), 864(m), 839(m), 820(m), 718(s), 679(s), 548(m), 468(m). Anal. Calc. for $C_{54}H_{42}CoN_2O_{12}Zn_2$ (1100.57), 1: C, 58.92; H, 3.85; N, 2.55. Found: C, 58.73; H, 3.80; N, 2.81%. Preparation of **2**: 18.2 mg (0.06 mmol) of $Zn(NO_3)_2$ hexahydrate, 18.8 mg (0.06 mmol) of $Cd(NO_3)_2$ tetrahydrate and 34.0 mg (0.24 mmol) of ammonium benzoate were dissolved in 4 mL H_2O and carefully layered by 4 mL acetonitrile solution of 1,2-bis(4-pyridyl)ethane ligand (11.1 mg, 0.06 mmol). Suitable crystals of compound **2** for X-ray analysis were obtained in three weeks. Compound **2** was stable below 260 °C from thermal gravimetric analysis (TGA). IR (KBr): $\nu(\mathrm{cm}^{-1}) = 3436$(brm), 3064(w), 2929(m), 2362(m), 1604(s), 1565(s), 1398(s), 1229(w), 1175(w), 1070(w), 1028(w), 839(w), 858(w), 819(w), 719(s), 688(m), 546(w), 452(m). Anal. Calc. for $C_{54}H_{42}CdN_2O_{12}Zn_2$ (1154.04), 2: C, 56.20; H, 3.68; N, 2.43. Found: C, 55.95; H, 3.55; N, 2.67%. Preparation of **3**: 17.8 mg (0.06 mmol) of $Co(NO_3)_2$ hexahydrate, 18.8 mg (0.06 mmol) of $Cd(NO_3)_2$ tetrahydrate and 34.0 mg (0.24 mmol) of ammonium benzoate were dissolved in 4 mL H_2O and carefully layered by 4 mL methanol solution of 1,2-bis(4-pyridyl)ethane ligand (11.1 mg, 0.06 mmol). Suitable crystals of compound **3** for X-ray analysis were obtained in four weeks. Compound **3** was stable below 350 °C from thermal gravimetric analysis (TGA). IR (KBr): $\nu(\mathrm{cm}^{-1}) = 3064$(w), 2950(w), 1599(s), 1558(s), 1399(s), 1165(w), 1135(w), 1069(w), 10260(m), 862(m), 835(w), 719(s), 690(m), 546(m), 451(m). Anal. Calc. for $C_{54}H_{42}CdCo_2N_2O_{12}$ (1141.16), 3: C, 56.83; H, 3.72; N, 2.46. Found: C, 56.91; H, 3.54; N, 2.66%.

[8] Crystal data for **1**: $C_{54}H_{42}CoN_2O_{12}Zn_2$, $M = 1100.57$, triclinic, $a = 10.318(2)$ Å, $b = 11.079(2)$ Å, $c = 13.102(3)$ Å, $\alpha = 76.00(3)°$, $\beta = 67.21(3)°$, $\gamma = 64.74(3)°$, $V = 1243.5(4)$ Å^3, $Z = 1$, μ(Mo Kα) = 1.352 mm^{-1}, 7035 reflections measured, 4789 unique ($R_{\mathrm{int}} = 0.0413$) which were used in all calculations, final $R = 0.0322$ ($wR = 0.0809$) with reflections having intensities greater than 2σ, GOF(F^2) = 0.948. Crystal data for **2**: $C_{54}H_{42}CdN_2O_{12}Zn_2$, $M = 1154.04$, triclinic, $a = 10.2658(14)$ Å, $b = 11.0981(15)$ Å, $c = 13.2738(18)$ Å, $\alpha = 76.787(2)°$, $\beta = 67.724(2)°$, $\gamma = 64.247(2)°$, $V = 1256.7(3)$ Å^3, $Z = 1$, μ(Mo Kα) = 1.430 mm^{-1}, 7099 reflections measured, 4832 unique ($R_{\mathrm{int}} = 0.1195$) which were used in all calculations, final $R = 0.0420$ ($wR = 0.0776$) with reflections having intensities greater than 2σ, GOF(F^2) = 0.803. Crystal data for **3**: $C_{54}H_{42}CdCo_2N_2O_{12}$, $M = 1141.16$, triclinic, $a = 10.457(2)$ Å, $b = 10.969(2)$ Å, $c = 13.194(3)$ Å, $\alpha = 73.124(4)°$, $\beta = 67.707(3)°$, $\gamma = 63.577(3)°$, $V = 1240.4(4)$ Å^3, $Z = 1$, μ(Mo Kα) = 1.151 mm^{-1}, 6579 reflections measured, 4602 unique ($R_{\mathrm{int}} = 0.0264$) which were used in all calculations, final $R = 0.0805$ ($wR = 0.2489$) with reflections having intensities greater than 2σ, GOF(F^2) = 1.052. Structural information was deposited at the Cambridge Crystallographic Data Center (CCDC reference numbers 744691 for **1**, 744692 for **2** and 744693 for **3**). The X-ray diffraction data for all three compounds were collected on a Bruker SMART APX diffractometer equipped with a monochromater in the Mo Kα ($\lambda = 0.71073$ 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. All hydrogen atoms were placed in the calculated positions. The crystallographic data for compounds **1–3** are listed in Table S1. The selected bond distances and angles are listed in Table S2.

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