DOI: 10.1002/ejic.200700823

Construction of Zn^{II} Compounds with a Chelating 2,2′-Dipyridylamine (Hdpa) Ligand: Anion Effect and Catalytic Activities

Han Kwak,[a] Sun Hwa Lee,[a] Soo Hyun Kim,[a] Young Min Lee,[a] Eun Yong Lee,[a] Byeong Kwon Park,[a] Eun Young Kim,[a] Cheal Kim,*[a] Sung-Jin Kim,[b] and Youngmee Kim*[b]

Keywords: Amines / Nitrogen heterocycles / Anion effects / Transesterification / Catalytic activities / Zinc

The structures of new compounds containing Zn^{II} ions and Hdpa (2,2′-dipyridylamine)-chelating ligands were determined. The Hdpa chelating ligands coordinate to Zn^{II} ions to form mononuclear units (**1** and **5**), and intermolecular nonclassical hydrogen-bond (C–H···O or N/C–H···I) interactions generate polymeric compounds. The chelating ligands with a bipyridyl moiety form mostly mononuclear complexes of different types (I, II and III), and the combination of this ligand with a sulfate anion can produce polymeric species (Type IV). Interestingly, homogeneous catalyst **1** catalyzed efficiently the transesterification of a variety of esters with different alcohols, and hydrogen-bonded polymer **5** showed the heterogeneous catalytic activity for the transesterification reactions. Preliminary selectivity test of primary over secondary alcohol protection in the presence of **1** provided, exclusively, the primary acetate, which suggests the potential utility of this catalyst to be selective for primary alcohols.

Introduction

There has been much attention on the role played by noncovalent interactions,[1] such as classical (N/O–H···N/O) and nonclassical hydrogen bonding [C–H···X (X = halide) or C–H···N/O/C], as well as anion effects[2] in the construction of molecular packing and crystal structures, as they can provide a good structural motif for the construction of a polymeric compound from a simple building block.[1,2] We and others have previously shown that 2,2′-dipyridylamine (Hdpa) as a chelating ligand mostly formed mononuclear Zn^{II} complexes [zinc salts used: $Zn(CN)_2$, $Zn(O_2CCH_3)_2$, $Zn(O_2C_6H_5)_2$, $Zn(ClO_4)_2$, $Zn(BF_4)_2$, $ZnCl_2$, $ZnBr_2$, and $Zn(CF_3SO_3)_2$],[3] and then these Zn^{II} complexes can be used as building blocks for the construction of polymeric compounds through weak hydrogen bonds and π–π interactions. However, the chelating ligand 2,2′-dipyridylamine (Hdpa) unexpectedly forms a polymeric compound with $ZnSO_4$.[3d] These results demonstrated that both anion effect and intermolecular hydrogen bonds are very important roles for the formation of polymeric or monomeric compounds. Moreover, the coordination polymer $[Zn(Hdpa)(H_2O)_2(SO_4)]$ and hydrogen-bonded polymers $[Zn(Hdpa)Br_2]$ and $[Zn(Hdpa)Cl_2]$ have shown, surprisingly, unusual heterogeneous catalytic activities in the transesterification reactions of esters.[3d]

Transesterification reactions are important transformations in organic synthesis in industrial as well as in academic laboratories.[4] There are many catalysts available for transesterification, and the most common procedure is to heat the ester with a catalytic amount of $Ti(O\textit{i}Pr)_4$ in an alcohol solvent at reflux.[5] Other Lewis acid catalysts such as $BuSn(OH)_3$ and $Al(OR)_3$ also catalyze this conversion. Transesterifications catalyzed by $Ti(O\textit{i}Pr)_4$ and $BuSn(OH)_3$ require higher reaction temperatures and acidic conditions.[6] Such drawbacks experienced with these catalysts drove us to develop new catalysts that operate under milder conditions.

As a part of our continued interests in the syntheses, structures, and reactivities of coordination complexes of Zn^{II} with chelating Hdpa ligands, and with the aim to fully understand the anion effect of our earlier work in order to find efficient catalysts to mediate various catalytic reactions that could be carried out under mild reaction conditions, we employed two more zinc salts with different counteranions (NO_3^- and I^-) to develop new complexes. Herein we report the syntheses, crystal structures, and reactivities of two new Zn-containing compounds formed by the reaction of the chelating Hdpa ligand and two different zinc salts. With the iodide anion, Zn^{II} produces a Type I mononuclear complex, and with the NO_3^- anion, Zn^{II} produces a Type III mono-

---

[a] Department of Fine Chemistry, and Eco-Product and Materials Education Center, Seoul National University of Technology,
Seoul 139-743, Korea
Fax: +82-2-973-9149
E-mail: chealkim@snut.ac.kr
[b] Division of Nano Sciences, Ewha Womans University
Seoul 120-750, Korea
Fax: +82-2-3277-2384
E-mail: ymeekim@ewha.ac.kr

Supporting information for this article is available on the WWW under http://www.eurjic.org or from the author.

nuclear complex. In both cases, intermolecular hydrogen bonds generate polymeric compounds. We also reported that homogeneous catalyst **1** catalyzed efficiently the transesterification of a variety of esters with different alcohols and that hydrogen-bonded polymer **5** showed heterogeneous catalytic activity for the transesterification reactions. Importantly, the transesterification reaction catalyzed by catalyst **1** is best among the catalytic systems reported previously in Zn-containing coordination and polymeric compounds, to the best of our knowledge, and heterogeneous hydrogen-bonded polymer **5** is only the third example of a catalyst used in heterogeneous transesterification reactions of various *p*-substituted phenyl acetates and benzoates under mild conditions.

Results and Discussion

The structures of compounds **1** and **5** were determined by X-ray crystallography. The Hdpa chelating ligands coordinate to the Zn^{II} ions to form mononuclear units, and intermolecular hydrogen-bond interactions such as classical (N/O–H···N/O) and nonclassical hydrogen bonding [C–H···X (X = halide) or C–H···N/O/C] generate polymeric compounds. Tables 1 and 2 list the selected bond lengths and angles for these structures.

Table 1. Selected bond lengths [Å] and angles [°] for compound **1**.

Zn1–N11	2.0654(17)	Zn1–N13	2.1242(18)
Zn1–N21	2.0675(18)	Zn1–O2	2.2085(16)
Zn1–N23	2.1093(19)	Zn1–O1	2.3183(17)
N11–Zn1–N21	107.09(7)	N11–Zn1–N23	97.69(7)
N21–Zn1–N23	87.97(7)	N21–Zn1–N23	87.97(7)
N21–Zn1–N23	87.97(7)	N11–Zn1–N13	87.65(7)
N21–Zn1–N13	98.96(7)	N23–Zn1–N13	169.66(7)
N11–Zn1–O2	100.89(6)	N21–Zn1–O2	151.97(6)
N23–Zn1–O2	86.67(6)	N13–Zn1–O2	83.61(6)
N11–Zn1–O1	157.81(7)	N21–Zn1–O1	95.05(7)
N23–Zn1–O1	84.32(6)	N13–Zn1–O1	87.42(6)
O2–Zn1–O1	57.04(6)		

Table 2. Selected bond lengths [Å] and angles [°] for compound **5**.

Zn1–N1[a]	2.013(4)	Zn1–N1	2.013(4)
Zn1–I1[a]	2.5669(8)	Zn1–I1	2.5669(8)
N1[a]–Zn1–N1	93.9(3)	N1[a]–Zn1–I1[a]	112.46(13)
N1–Zn1–I1[a]	112.47(13)	N1[a]–Zn1–I1	112.47(13)
N1–Zn1–I1	112.46(13)	I1[a]–Zn1–I1	111.91(4)

[a] Symmetry transformations used to generate equivalent atoms: $-x + 1, y, -z + 1/2$.

Crystal Structure of $[Zn(Hdpa)_2(NO_3)](NO_3)$ (1)

The asymmetric unit consists of a whole molecule containing a zinc(II) ion, two Hdpa ligands, a nitrate ligand, and a nitrate counteranion. Two Hdpa ligands and a nitrate ligand coordinate to a Zn^{II} ion to form a six-coordinate

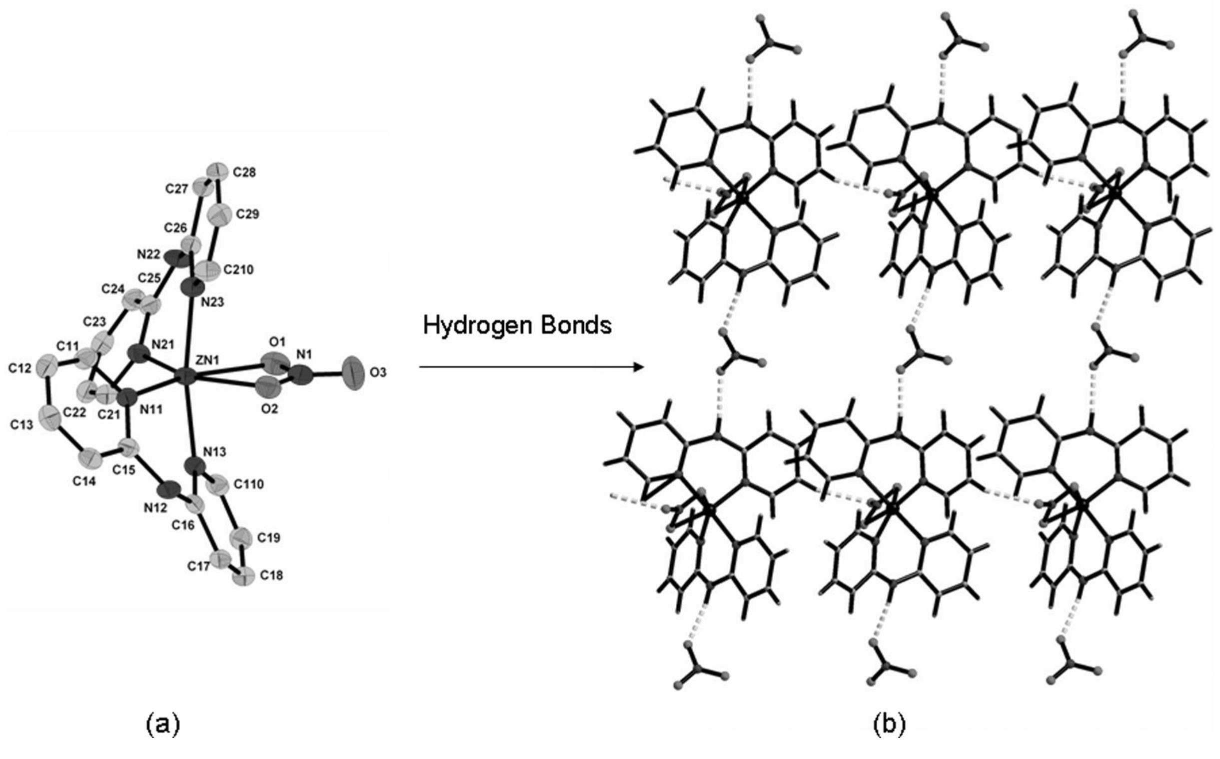


Figure 1. (a) Structure of $[Zn(Hdpa)_2(NO_3)](NO_3)$ **1** with 50% ellipsoids. All hydrogen atoms are omitted for clarity; (b) 2D polymeric structure derived by hydrogen bonds. Hydrogen bond lengths (angles): H12N···O32 ($x, 1.5 - y, -0.5 + z$) 2.022(3) Å [N12–H12N–O32 171.02(2)°], H22N···O33 ($1 + x, y, z$) 1.932(4) Å [N22–H22N–O33 170.86(2)°], H12···O3 ($x, 1.5 - y, -0.5 + z$) 2.472(2) Å [C12–H12–O3 157.09(1)°].

Zn^{II} complex with a N23–Zn1–N13 angle of 169.66° (Figure 1a). The $Zn–N_{pyridyl}$ bond lengths range from 2.0654(17) to 2.1242(18) Å, which are typical for Zn^{II} compounds with Hdpa,[3] and the $Zn–O_{nitrate}$ bond lengths are 2.2085(16) and 2.3183(17) Å (Table 1). Two pyridyl rings are bent with torsion angles C24–C25–N22–C26 and C14–C15–N12–C16 of 169.29(1) and 150.22(1)°, respectively. There are hydrogen bonds between an amine hydrogen atom and a nitrate oxygen atom ($N–H\cdots O–N_{nitrate}$) and between a coordinated nitrate oxygen atom and a neighboring pyridyl hydrogen atom ($C_{pyridyl}–H\cdots O–N_{nitrate}$), and these hydrogen bonds generate a 2D polymeric compound (Figure 1b). The $H\cdots O_{nitrate}$ distances of 1.932(4) and 2.022(3) Å and the N–H···O angles of 170.86(2) and 171.02(2)° indicate the formation of N–H···O hydrogen bonds, and the $H\cdots O_{nitrate}$ distance of 2.471(2) Å and the $C_{pyridyl}–H\cdots O$ angle of 157.09(1)° indicate the formation of C–H···O hydrogen bonds.[1] In the 2D structure, the Zn···Zn distance is 8.195(1) Å.

Crystal Structure of [Zn(Hdpa)(I_2)] (5)

The asymmetric unit consists of half of a molecule, and a mirror plane is located in the middle of the molecule. The complete compound structure is generated by the symmetry operation (–*x* + 1, *y*, –*z* + 1/2) as shown in Figure 2a. The $Zn–N_{pyridyl}$ bond length is 2.013(4) Å, which is also typical for Zn^{II} compounds with Hdpa,[3] and the Zn–I bond length is 2.5669(8) Å (Table 2). There are nonclassical hydrogen bonds between the I atoms and the pyridyl hydrogen atoms (Zn–I···H–N) and between the I atoms and the amine hydrogen atoms (Zn–I···H–C). These interactions further extend this mononuclear complex into a 2D architecture (Figure 2b). The H···I distance of 3.162(2) Å and the N–H···I angle of 137.73(1)° indicate the formation of N–H···I hydrogen bonds, and the H···I distance of 3.249(3) Å and the C–H···I angle of 145.86(1)° indicate the formation of C–H···I hydrogen bonds.[7] The importance of such C–H···I hydrogen bonds in the supramolecular self-assembly was also reported recently.[7c,8] Self-assembly of discrete metal complexes by weak C–H···I–Zn interactions was reported,[9] although intermolecular C–H···I interactions do exist in a few compounds.[7c,8] This is only the second example of self-assembly of Zn–I···H–C nonclassical H-bonding interactions.[9] Moreover, Zn–I···H–N hydrogen bonding is a rare case.[7d] The Zn^{II} ion has a distorted tetrahedral geometry with a I–Zn–I angle of 111.91(4)°. Two pyridyl rings are nearly coplanar with the torsion angle C1–N1–Zn1–N1 (1 – *x*, *y*, 0.5 – *z*) of –179.8(1)°.

Hdpa has been used as a chelating ligand to mostly form mononuclear Zn^{II} complexes. Previously, we showed the anion effects on construction of Zn^{II} polymeric compounds containing chelating Hdpa ligands.[3] Structure variation according to anions is shown in Scheme 1.

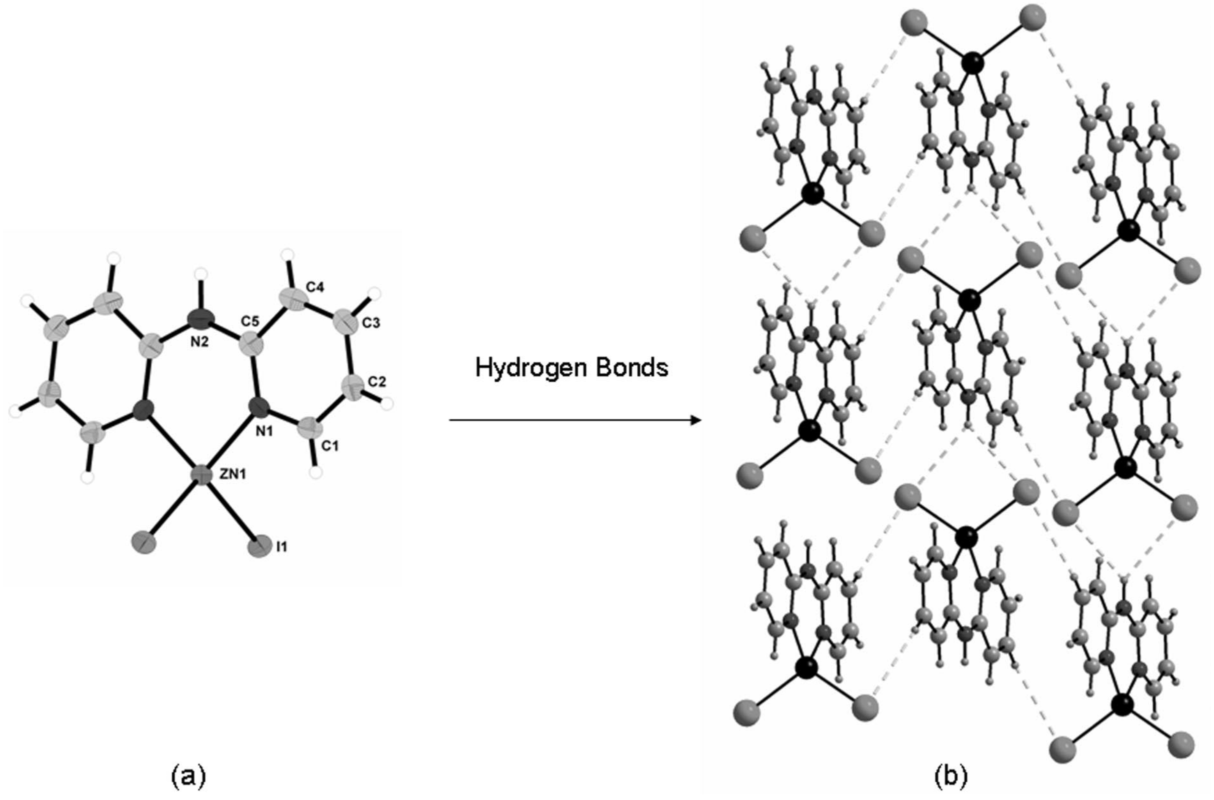
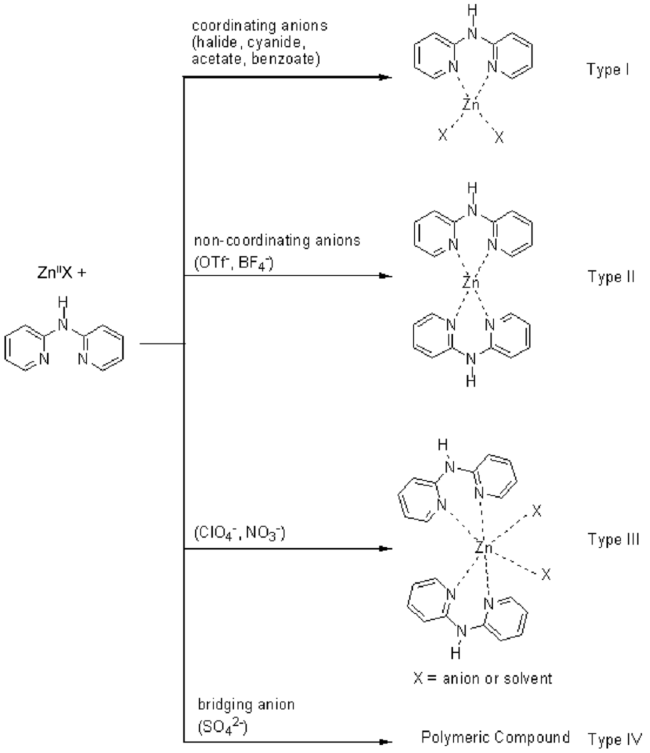


Figure 2. (a) Structure of [Zn(Hdpa)I_2] **5** with 50% ellipsoids; (b) 2D polymeric structure derived by nonclassical hydrogen bonds between I atoms and pyridyl hydrogen atoms and amine hydrogen atoms. Hydrogen bond lengths (angles): N2–H2N···I1(*x*, –1 + *y*, *z*) 3.162(2) Å [N2–H2N–I1 137.73(1)°], C3–H3···I1 (0.5 – *x*, 1.5 – *y*,–*z*) 3.249(3) Å [C3–H3–I1 145.86(1)°].



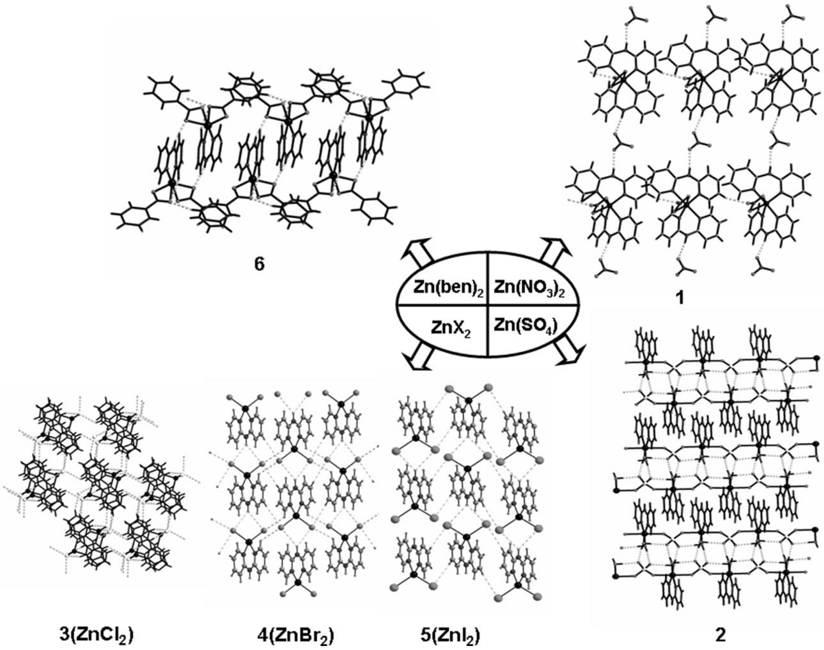
Scheme 1. Structure types according to anions.

With coordinating halide, cyanide, acetate, and benzoate anions, Zn^{II} produced distorted tetrahedral mononuclear complexes (Type I) with two nitrogen donor atoms of Hdpa and two coordinating anions.[3a] With noncoordinating OTf^-, BF_4^-, and ClO_4^- anions, Zn^{II} also produced mononuclear complexes but containing two Hdpa ligands with distorted tetrahedral (Td) (Type II), flattened tetrahedral (Td) (Type II), and six-coordinate geometries (Type III), respectively.[3b,3c] For bridging SO_4^{2-} anions, surprisingly, Zn^{II} produced a polymeric compound (Type IV).[3d] To fully understand anion effects for Zn^{II} complexes containing Hdpa, two more Zn^{II} salts containing iodide and nitrate anions were used. With the iodide ligand, Zn^{II} produces a Type I structure, and with the NO_3^- anion, Zn^{II} produces a Type III structure. Importantly, these results suggest that the chelating ligands with a bipyridyl moiety form mostly mononuclear complexes of different types (I, II and III), and the combination of this ligand with a sulfate anion can produce polymeric species (Type IV); thus, intermolecular hydrogen bonds as well as anion effects play very important roles in the construction of polymeric crystal structures.

Homogeneous Catalytic Activity of Compound 1

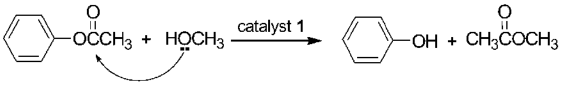
As part of our efforts to develop transesterification catalysts based on metal ions that are not redox active, we previously reported that Zn-containing coordination polymer **2** and hydrogen-bonded polymers **3** and **4** could carry out the heterogeneous catalytic transesterification of a range of esters with methanol at room temperature under mild conditions (see Scheme 2 for structures of six compounds as transesterification catalysts), whereas compound **6** [(Hdpa)-$Zn(benzoate)_2$] did catalyze the homogeneous transesterification reactions.[3d] In addition, heterogeneous catalyst **2** has shown even better catalytic activity than homogeneous catalyst **6**.

This catalyst system constitutes a promising class of heterogeneous catalysts that allowed reuse without any loss of activity through 10 runs with ester and appears to be an



Scheme 2. Structures of six compounds containing chelating Hdpa ligands as transesterification catalysts.

efficient, mild, and easily recyclable method for the alcoholysis of esters. On the basis of previous results, compound **1** has also been employed as a homogeneous catalyst in transesterification owing to its high solubility in methanol. The ester, phenyl acetate, was initially used as a substrate [Equation (1)].



(1)

We observed that **1** catalyzed the reaction of methanol with phenyl acetate, with quantitative conversion to methyl acetate in 0.25 d (Table 3, Entry 3) at room temperature under the neutral conditions. Because there is the possibility that the zinc salt [$Zn(NO_3)_2$] leached from compound **1** can promote transesterification, we carried out the control experiment of some esters with $Zn(NO_3)_2$ as shown in the previous study.[2e] The transesterification reaction of phenyl acetate in the presence of $Zn(NO_3)_2$ was very slow (50 d compared to 0.25 d for complex **1**), which indicates that the zinc salt does not have any influence in our catalytic systems. Importantly, this result is the best among the catalytic systems reported previously in Zn-containing coordination and polymeric compounds,[2e,2f,3d,10] to our best knowledge. Once having established that **1** represents an excellent catalyst for the transesterification reaction of phenyl acetate with methanol, we investigated the transesterification of various *p*-substituted phenyl acetates and benzoates. The substrates with electron-withdrawing substituents underwent fast transesterification (Table 3, Entries 1, 5, and 6), whereas those with electron-donating groups underwent slow transesterification (Table 3, Entries 4 and 8). *p*-Nitrophenyl acetate and *p*-nitrophenyl benzoate with nitro substituents in the *para* position, which are known to be problematic substrates for the transesterification reaction due to undesirable side reactions such as isomerization or polymerization,[11] were also converted quantitatively into the corresponding products.

In a certain case, transesterification of esters with alcohol cannot achieve high conversions because of the reversibility of the reaction. However, this problem can be solved by using enol esters as acylating agents, as the resultant enolate is converted into an aldehyde or ketone that is unable to participate in the reverse reaction.[12] Therefore, vinyl acetate was used as an example and, expectedly, converted efficiently into the product methyl acetate within 0.17 d by **1** (Table 3, Entry 9), which suggests that this catalytic system can be useful for the preparation of various esters by transesterification.

On the basis of this promising result, transesterification with the more challenging nucleophiles ethanol, 2-propanol, and propanol was tested with phenyl acetate. Whereas the reaction of phenyl acetate with either ethanol (60 d; data not shown) or 2-propanol (60 d; data not shown) was very slow, propanol drove the reaction to completion within 5 d (Table 3). Various esters were also examined with propanol as a nucleophile. The substrates with electron-withdrawing substituents underwent fast conversion into the corresponding products, whereas those with the electron-donating ones underwent slow transesterification.

Protection of a primary alcohol in the presence of a secondary alcohol is useful in natural product synthesis.[4a,13] Therefore, selectivity of primary over secondary alcohol protection was tested. In a mixture of propanol and 2-propanol (1/1) in the presence of **1** and phenyl acetate, only the reaction of propanol proceeded and propyl acetate was obtained in 99.9% yield, whereas the secondary acetate was formed in <0.1% yield. This reaction suggests the potential utility of our catalyst for the selective protection of primary alcohols.

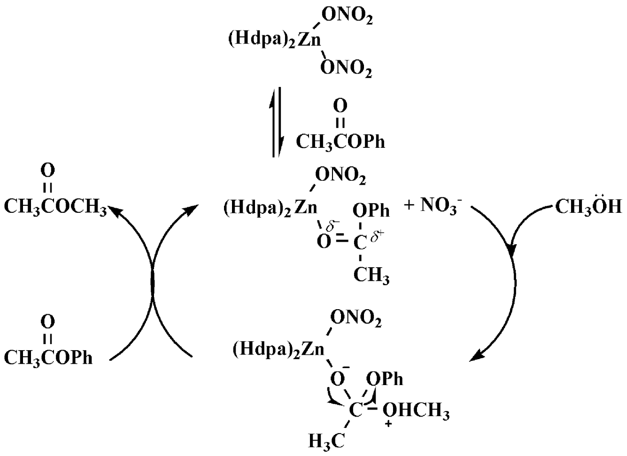
It was proposed that the mechanism of metal-ion-catalyzed transesterification probably involves electrophilic activation of the carbon center of the carbonyl moiety by binding of the metal to the carbonyl oxygen; hence, Lewis acidity of the metal center may be important in catalytic transesterification.[14] On the basis of this idea, a possible transesterification mechanism in this catalyst system can be proposed (Scheme 3). The phenyl acetate substrate substitutes an anion (NO_3^-) to give the adduct $(Hdpa)_2Zn(NO_3)(Sub)$.

Table 3. Transesterfication of esters by alcohol in the presence of the compounds **1** and **5** at room temperature.[a]

Entry	Substrate	**1** (Homo in methanol)[b] Time [d]	**1** (Homo in propanol)[b] Time [d]	**5** (Hetero in methanol)[c] Time [d]
1	4-Nitrophenyl acetate	0.17	5	4
2	4-Fluorophenyl acetate	4	–	–
3	Phenyl acetate	0.25	9	8
4	4-Methylphenyl acetate	3.9	–	–
5	4-Nitrophenyl benzoate[d]	1.3	36	33
6	4-Chlorophenyl benzoate	0.38	13	9
7	Phenyl benzoate	1	12	12
8	4-Methylphenyl benzoate	0.88	13	12
9	Vinyl acetate	0.17	8	5

[a] All esters were completely converted into the corresponding products, methyl acetate and methyl benzoate. Reaction conditions: esters 0.05 mmol, catalyst 2×10^{-3} mmol, solvent methanol or propanol (1 mL). See the Experimental Section for detailed reaction conditions. [b] Homo means homogeneous catalytic reaction conditions. [c] Hetero means heterogeneous catalytic reaction conditions. [d] The solvent was CH_3OH/CH_3CN (1:1) because of the low solubility of the substrate in CH_3OH.

Then, the methanol nucleophile would attack the carbon atom of carbonyl moiety of the adduct to produce the product methyl acetate. Detailed mechanistic studies are currently under investigation.



Scheme 3. Plausible transesterification mechanism.

Heterogeneous Catalytic Activity of Compound 5

We also examined the catalytic activity of heterogeneous hydrogen-bonded polymer **5** as a heterogeneous catalyst for the transesterification of phenyl acetate [Equation (1)], because it was insoluble in alcohol solvents. Treatment of phenyl acetate and methanol in the presence of **5**, which was ground well into appropriate sizes for high surface area but not too small for a convenient filtration,[15] produced quantitatively methyl acetate in 8 d at room temperature (Table 3, Entry 3). No or little transesterification occurs without polymeric compound **5**.

Because the potential benefits of the heterogeneous catalyst include easy separation of the catalyst from reagents and reaction products and recyclability for repeated use,[15] we examined the recovery and reuse of catalyst **5** at room temperature on the basis of our previous experience.[16] After the reaction with phenyl acetate was complete, the catalyst was recovered by filtration and thoroughly washed with methanol for the consecutive runs. The recovered catalyst was used for a new reaction batch of phenyl acetate. Catalyst **5** showed excellent recyclability for 10 times without showing any significant deterioration of catalytic activity (see Table S1 in the Supporting Information).

With the usefulness of the recyclability of catalyst **5** for efficient transesterification, we then checked for heterogeneity, because in the process of catalysis, the metal species leached from the catalysts might catalyze efficiently the transesterification reaction instead of the heterogeneous catalysts.[15,16] We filtered catalyst **1** after the transesterification reaction of phenyl acetate and allowed the filtered catalyst and the filtrate to react with another aliquot of phenyl acetate, as shown in the previous study.[15,16] We observed that the transesterification reaction with the filtered catalyst proceeded at the original rate, whereas the filtrate showed about 10% conversion within the same time interval. This result strongly suggests that the dominant reactive species is heterogeneous catalyst **1** and not other species such as the leached-out metal. On the other hand, the powder X-ray diffraction (XRD) pattern of filtered catalyst **5** after the reaction revealed the same pattern as that of original catalyst **5**, which suggests that the original structure of the filtered catalyst was maintained during the reaction (see Figure S1 in the Supporting Information). On the basis of these results, we concluded that heterogeneous hydrogen-bonded polymer **5** could be recycled multiple times without a significant loss in activity.

The transesterification of other esters including benzoates by catalyst **5** was also carried out efficiently and the results are given in Table 3. Catalyst **5** showed a similar trend to that of catalyst **1**. The substrates with electron-withdrawing substituents underwent fast transesterification, whereas those with electron-donating underwent slow reactions. Benzoates underwent slower transesterification than acetates. The problematic substrates for the transesterification reaction, *p*-nitrophenyl acetate and *p*-nitrophenyl benzoate with nitro substituents in the para position, were also converted quantitatively into the corresponding products. Moreover, an efficient acylating agent, vinyl acetate, was converted efficiently into the product methyl acetate within 5 d by **5** (Table 3, Entry 9), as the resultant enolate was converted into an aldehyde or ketone that was unable to participate in the reverse reaction.

At this moment, we do not know the exact reactive species or the reaction mechanism for the transesterification reaction by catalyst **5**. A detailed study on these topics is ongoing.

Conclusions

We showed two new structures of Zn^{II} complexes containing Hdpa ligands to complete the study of anion effects. ZnI_2 and $Zn(NO_3)_2$ produce mononuclear complexes with different types of structures. Zn^{II} produces four types of structures: with coordinating anions, Type I; with noncoordinating anions, Type II; with ClO_4^- and NO_3^-, Type III; with bridging sulfate anion, polymeric structure Type IV. These results indicate that an anion effect is very important for the construction of Zn^{II} complexes containing chelating Hdpa ligands, and intermolecular hydrogen bonds also play very important roles for the construction of polymeric crystal structures.

We also showed that homogeneous catalyst **1** catalyzed efficiently the transesterification of a variety of esters with different alcohols, and hydrogen-bonded polymer **5** showed heterogeneous catalytic activity for the transesterification reactions. Importantly, the transesterification reaction catalyzed by catalyst **1** is the best among the catalytic systems reported previously in Zn-containing coordination and polymeric compounds, to our best knowledge, and heterogeneous hydrogen-bonded polymer **5** is only the third example of a catalyst used in the heterogeneous transesterification of various *p*-substituted phenyl acetates and benzoates under mild conditions. Moreover, the scope of the application of **1** as a transesterification catalyst was expanded to now include ethanol and propanol. Furthermore, preliminary selectivity tests of primary over secondary alcohol protection in the presence of **1** and phenyl acetate has provided, exclusively, the primary acetate propyl acetate, which suggests the potential utility of our catalyst to be used in the selective protection of primary alcohols. Further explorations into the uses of this catalyst family in organic transformations as well as mechanistic investigations are ongoing.

Experimental Section

Materials: 2,2′-Dipyridylamine (Hdpa), methanol, ethanol, propanol, *para*-substituted phenyl acetate, *para*-substituted phenyl benzoate, methyl acetate, methyl benzoate, and zinc salts were purchased from Aldrich and were used as received. 4-Fluorophenyl acetate and 4-nitrophenyl benzoate were obtained from Lancaster.

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. Product analysis for the transesterification reaction was performed with either a Hewlett–Packard 5890 II Plus gas chromatograph interfaced with a Hewlett–Packard Model 5989B mass spectrometer or a Donam Systems 6200 gas chromatograph equipped with a FID detector with a 30-m capillary column (Hewlett–Packard, HP-1, HP-5, and Ultra 2). XRD data were obtained with a Rigaku X-ray diffractometer with Cu-K_α radiation (λ = 1.5418 Å).

$[Zn(Hdpa)_2(NO_3)](NO_3)$ (1): $Zn(NO_3)_2 \cdot 6H_2O$ (37.2 mg, 0.125 mmol) was dissolved in methanol (4 mL) and carefully layered by a solution of the 2,2′-dipyridylamine ligand (42.8 mg, 0.25 mmol) in acetone (4 mL). Suitable crystals of compound **1** for X-ray analysis were obtained in a few weeks. Yield: 43.1 mg (65.4 %). ^{1}H NMR (300 MHz, D_2O): δ = 6.79–7.25 (m, 8 H, aromatic-H). MS (ESI): *m*/*z* = 468 $[Zn(Hdpa)_2(NO_3)]^+$. IR (KBr): $\tilde{\nu}$ = 3313 (m), 3201 (m), 3074 (m), 3020 (br. s), 1650 (s), 1596 (s), 1582 (s), 1535 (s), 1480 (s), 1396 (s), 1315 (s), 1285 (s), 1236 (s), 1162 (s), 1052 (w), 1010 (s), 872 (m), 771 (s), 645 (m), 531 (m), 419 (m) cm^{-1}. $C_{20}H_{18}N_8O_6Zn$ (531.79): calcd. C 45.17, H 3.42, N 21.07; found C 45.34, H 3.39, N 20.89.

$[Zn(Hdpa)(I_2)]$ (5): ZnI_2 (31.9 mg, 0.1 mmol) was dissolved in H_2O (4 mL) and carefully layered with a solution of the 2,2′-dipyridylamine ligand (34.2 mg, 0.2 mmol) in acetone (2 mL), ethanol (1 mL), and methanol (1 mL). Suitable crystals of compound **5** for X-ray analysis were obtained in a few days. Yield: 32.8 mg (66.9 %). IR (KBr): $\tilde{\nu}$ = 3335 (s), 1636 (s), 1585 (s), 1523 (s), 1479 (s), 1434 (m), 1415 (w), 1231 (s), 1159 (s), 1021 (s), 909 (w), 772 (s), 653 (w), 564 (w), 519 (w), 418 (w) cm^{-1}. $C_{10}H_9I_2N_3Zn$ (490.37): calcd. C 24.49, H 1.85, N 8.57; found C 24.40, H 1.61, N 8.77.

Catalytic Transesterification Reaction Conditions: To a solution of the esters (0.05 mmol) dissolved in methanol (1 mL) was added the catalyst (2×10^{-3} mmol), and the mixture was shaken at room temperature (450 rpm). Reaction conversion was monitored by GC–MS 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. Yield was based on the formation of the products, methyl acetate, or methyl benzoate.

Crystallography: The diffraction data for compounds **1** and **5** were collected with a Bruker SMART AXS diffractometer equipped with a monochromator in the Mo-K_α (λ = 0.71073 Å) incident beam. The crystal was mounted on a glass fiber. The CCD data were integrated and scaled by using the Bruker-SAINT software package, and the structure was solved and refined by using SHEXTL V6.12.[17] Hydrogen atoms were located in the calculated positions. The crystallographic data for compounds **1** and **5** are listed in Table 4. CCDC-655108 and -655109 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.

Supporting Information (see footnote on the first page of this article): Recycle experiments for the transesterification reactions of phenyl acetate by heterogeneous catalyst **5** and PXRD data for before and after reaction of **5**.

Table 4. Crystallographic data for compounds **1** and **5**.

	1	**5**
Empirical formula	$C_{20}H_{18}N_8O_6Zn$	$C_{10}H_9I_2N_3Zn$
Formula weight	531.79	490.37
Temp. [K]	293(2)	293(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$ (no. 14)	$C2/c$ (no. 15)
a [Å]	14.897(3)	16.393(3)
b [Å]	9.7402(16)	7.9432(16)
c [Å]	16.259(3)	12.865(3)
β [°]	115.121(3)	128.296(3)
Volume [Å^3]	2444.5(8)	1314.7(5)
Z	4	4
Absorption coefficient [mm^{-1}]	1.208	6.541
No. of data collected	11581	3424
No. of unique data	4166	1261
$R_{int.}$	0.0470	0.0599
Goodness-of-fit	0.903	0.949
Final *R* indices [$I > 2\sigma(I)$]	R_1 = 0.0305, wR_2 = 0.0640	R_1 = 0.0365, wR_2 = 0.0911
Final *R* indices (all data)	R_1 = 0.0422, wR_2 = 0.0654	R_1 = 0.0427, wR_2 = 0.0926

Acknowledgments

Financial support from the Korean Science & Engineering Foundation [R01-2005-000-10490-0(2005)], the Korea Research Foundation (2006-312-C00569 and KRF-2004-005-C00093), and Seoul R&BD Program is gratefully acknowledged.

---

[1] a) X. J. Luan, Y.-Y. Wang, D.-S. Li, P. Liu, H.-M. Hu, Q.-Z. Shi, S.-M. Peng, *Angew. Chem. Int. Ed.* **2005**, *44*, 3864–3867; b) B.-B. Ding, Y.-Q. Weng, Z.-W. Mao, C.-K. Lam, X.-M. Chen, B.-H. Ye, *Inorg. Chem.* **2005**, *44*, 8836–8845; c) A. Angeloni, P. C. Crawford, A. G. Orpen, T. J. Podesta, B. J. Shore, *Chem. Eur. J.* **2004**, *10*, 3783–3791; d) V. Balamurugan, M. S. Hundal, R. Mukherjee, *Chem. Eur. J.* **2004**, *10*, 1683–1690; e) Y. Wang, J. Yu, Y. Li, Z. Shi, R. Xu, *Chem. Eur. J.* **2003**, *9*, 5048–5055; f) D. Braga, F. Grepioni, G. R. Desiraju, *Chem. Rev.* **1998**, *98*, 1375–1406; g) C. Janaik, T. G. Scharmann, *Polyhedron* **2003**, *22*, 1123–1133; h) L. Brammer, E. A. Bruton, P. Sherwood, *Cryst. Growth Des.* **2001**, *1*, 277–290; i) G. R. Desiraju, *Acc. Chem. Res.* **2002**, *35*, 565–573.

[2] a) L. Carlucci, G. Ciani, D. M. Proserpio, S. Rizzato, *Chem. Eur. J.* **1999**, *5*, 237–243; b) H.-P. Wu, C. Janiak, G. Rheinwald, H. Lang, *J. Chem. Soc. Dalton Trans.* **1999**, 183–190; c) Z. Ni, J. Vittal, *Cryst. Growth Des.* **2001**, *1*, 195–197; d) M. Du, X.-H. Bu, Y.-M. Guo, H. Liu, S. R. Batten, J. Ribas, T. C. W. Mak, *Inorg. Chem.* **2002**, *41*, 4904–4908; e) J. Y. Ryu, J. H. Han, J. Y. Lee, S. J. Hong, S. H. Choi, C. Kim, S.-J. Kim, Y. Kim, *Inorg. Chim. Acta* **2005**, *358*, 3659–3670; f) Y. Kim, S.-J. Kim, S. H. Choi, J. H. Han, S. H. Nam, J. H. Lee, H. J. Kim, C. Kim, D. W. Kim, H. G. Jang, *Inorg. Chim. Acta* **2006**, *359*, 2534–2542.

[3] a) K.-Y. Ho, W.-Y. Yu, K.-K. Cheung, C.-M. Che, *Chem. Commun.* **1998**, 2101–2102; b) K.-Y. Ho, W.-Y. Yu, K.-K. Cheung, C.-M. Che, *J. Chem. Soc. Dalton Trans.* **1999**, 1581–1586; c) Y. Gultneh, A. R. Khan, D. Blaise, S. Chaudhry, B. Ahvazi, B. B. Marvey, R. J. Butchre, *J. Inorg. Biochem.* **1999**, *75*, 7–18; d) Y. M. Lee, S. J. Hong, H. J. Kim, S. H. Lee, H. Kwak, C. Kim, S.-J. Kim, Y. Kim, *Inorg. Chem. Commun.* **2007**, *10*, 287–291.

[4] a) M.-H. Lin, T. V. RajanBabu, *Org. Lett.* **2000**, *2*, 997–1000; b) G. A. Grasa, R. M. Kissling, S. P. Nolan, *Org. Lett.* **2002**, *4*, 3583–3586; c) G. A. Grasa, T. Guveli, R. Singh, S. P. Nolan, *J. Org. Chem.* **2003**, *68*, 2812–2819.

[5] D. Seebach, E. Hungerbuhler, R. Naef, D. Schnurrenberger, B. Weidmann, M. Zuger, *Synthesis* **1982**, 138–140.

[6] a) R. L. E. Furlan, E. G. Mata, O. A. Mascaretti, *Tetrahedron Lett.* **1998**, *39*, 2257–2260; b) C. E. Rehberg, C. H. Fisher, *J. Org. Chem.* **1947**, *12*, 226–231.

[7] a) C. J. Horn, A. J. Blake, N. R. Champness, A. Garau, V. Lippolis, C. Wilson, M. Schröder, *Chem. Commun.* **2003**, 312–313; b) C. Horn, M. Scudder, I. Dance, *CrystEngComm* **2001**, *1*, 1–8; c) G. Barberà, C. Viñas, F. Teixidor, G. M. Rosair, A. J. Welch, *J. Chem. Soc. Dalton Trans.* **2002**, 3647–3648; d) R. Custelcean, T. J. Haverlock, B. A. Moyer, *Inorg. Chem.* **2006**, *45*, 6446.

[8] L.-Y. Kong, Z.-H. Zhang, T. A. Okamura, M.-J. Fei, W.-Y. Sun, N. Ueyama, *Chem. Lett.* **2004**, *33*, 1572–1573.

[9] L. Han, H. Valle, X. Bu, *Inorg. Chem.* **2007**, *46*, 1511–1513.

[10] a) J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon, K. Kim, *Nature* **2000**, *404*, 982–986; b) J. Y. Lee, S. J. Hong, C. Kim, S.-J. Kim, Y. Kim, *Inorg. Chem. Commun.* **2005**, *8*, 692–696.

[11] V. K. Aggarwal, A. Mereu, *Chem. Commun.* **1999**, 2311–2312.

[12] a) G. A. Grasa, R. M. Kissling, S. P. Nolan, *Org. Lett.* **2002**, *4*, 3583–3586; b) G. W. Nyce, J. A. Lamboy, E. F. Connor, R. M. Waymouth, J. L. Hedrick, *Org. Lett.* **2002**, *4*, 3587–3590; c) D. Tashiro, Y. Kawasaki, S. Sakaguchi, Y. Ishii, *J. Org. Chem.* **1997**, *62*, 8141–8144; d) Y. Ishii, M. Takeno, Y. Kawasaki, Y. Muromachi, Y. Nishiyama, S. Sakaguchi, *J. Org. Chem.* **1996**, *61*, 3088–3092.

[13] A. Orita, A. Mitsutome, J. Otera, *J. Org. Chem.* **1998**, *63*, 2420–2421.

[14] a) J. Weston, *Chem. Rev.* **2005**, *105*, 2151–2174; b) G. Parkin, *Chem. Rev.* **2004**, *104*, 699–767.

[15] a) M. Fujita, Y. J. Kwon, S. Washizu, K. Ogura, *J. Am. Chem. Soc.* **1994**, *116*, 1151–1152; b) M. Fujita, K. Umemota, M. Yoshizawa, N. Fujita, T. Kusukawa, K. Biradha, *Chem. Commun.* **2001**, 509–518; c) S.-K. Yoo, J. Y. Ryu, J. Y. Lee, C. Kim, S.-J. Kim, Y. Kim, *Dalton Trans.* **2003**, 1454–1456; d) S. J. Hong, J. Y. Ryu, J. Y. Lee, C. Kim, S.-J. Kim, Y. Kim, *Dalton Trans.* **2004**, 2697–2701; e) H. Han, S. Zhang, H. Hou, Y. Fan, Y. Zhu, *Eur. J. Inorg. Chem.* **2006**, 1594–1600; f) K. Ding, Z. Wang, X. Wang, Y. Liang, X. Wang, *Chem. Eur. J.* **2006**, *12*, 5188–5197.

[16] a) S. H. Lee, E. Y. Lee, D.-W. Yoo, S. J. Hong, J. H. Lee, H. Kwak, Y. M. Lee, J. Kim, C. Kim, J.-K. Lee, *New J. Chem.* **2007**, *31*, 1579–1582; b) D.-W. Yoo, S.-K. Yoo, C. Kim, J.-K. Lee, *J. Chem. Soc. Dalton Trans.* **2002**, 3931–3932; c) D.-W. Yoo, J.-H. Han, S. H. Nam, H. J. Kim, C. Kim, J.-K. Lee, *Inorg. Chem. Commun.* **2006**, *9*, 654–657.

[17] Bruker, *SHELXTL/PC*, Version 6.12 for Windows XP, Bruker AXS Inc., Madison, Wisconsin, USA, **2001**.

Received: August 6, 2007