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Anion effects on construction of Zn^{II} compounds with a chelating ligand bis(2-pyridylmethyl)amine and their catalytic activities

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ABSTRACT

Three Zn^{II} complexes containing bispicam ligands (bispicam = bis(2-pyridylmethyl)amine), $[Zn(bispicam)_2](NO_3)_2{\cdot}2CH_3OH$ **4A**, $[Zn(bispicam)(NO_3)_2]$ **4B**, and $[Zn(bispicam)_2](OTf)_2$ **6**, were obtained, and their structures were determined by X-ray crystallography. Complexes of the general formulation $[Zn(bispicam)_2]X_2$ ($X = Cl^-$ (**1**), Br^- (**2**), I^- (**3**), NO_3^- (**4A**), ClO_4^- (**5**), and OTf^- (**6**)) show *fac* geometric isomers (a) or enantiomers (c) and (d) according to anions. Moreover, complexes **4**–**6** could carry out the catalytic transesterification of a range of esters with methanol under the mild conditions. Importantly, the catalyst **4B** with an unsaturated structure has shown better efficiency than the catalysts, **4A**, **5**, and **6**, having saturated structures. To explain this reactivity difference, two different reaction mechanisms have been proposed (metal-based *vs.* amide N–H-based).

1. Introduction

Self-assembly process for construction of coordination networks [1–6] has been affected by the hydrogen bonds [7–13], π–π stacking [14], and anions [15–19] as well as ligand design [20] and coordination numbers [21,22]. Among them, anion effect is a very important role for the self-assembled construction when anions can be coordinated to the metal centers. For examples, we have, quite recently, shown the anion effects on construction of Zn^{II} polymeric compounds containing chelating Hdpa (2,2-dipyridylamine) ligands [23,24]. With coordinating halide, cyanide, acetate, and benzoate anions, Zn^{II} produced distorted tetrahedral mononuclear complexes with two nitrogen donor atoms of Hdpa and two coordinating anions. With non-coordinating $SO_3CF_3^-$ (OTf^-), BF_4^- and ClO_4^- anions, Zn^{II} produced also mononuclear complexes containing two Hdpa ligands with distorted tetrahedral, flattened tetrahedral, and six-coordinated geometries, respectively. For the bridging SO_4^{2-} anion, surprisingly, Zn^{II} produced a polymeric compound that shows a heterogeneous catalytic reactivity [23].

Bis(2-pyridylmethyl)amine (bispicam) is a tridentate ligand where the two terminal N-donor coordination sites (pyridyl) are identical each other, but different from the central N-donor site (amine). Two bispicam ligands can coordinate to metal ion to provide complexes of the general formulation $[M(bispicam)_2]X_2$. For this type of complex system, three potential geometric isomers are shown in Scheme 1 (a–d). Among them, (b) isomer is the meridional isomer while the others are facial, and (c) and (d) are enantiomers [25]. In our previous study, three Zn^{II} complexes ($[Zn(bispicam)_2]Cl_2$ **1**, $[Zn(bispicam)_2]Br_2$ **2** and $[Zn(bispicam)_2]I_2$ **3**) were obtained [25,26]. Only facial isomer (a) was isolated, and there were hydrogen bonding interactions between N_{amine}–H and C–H of $[Zn(bispicam)_2]^{2+}$ cations and free halides, and between O_{water}–H and free halide for construction of molecular packing and crystal structures [26].

In addition, these hydrogen-bonded complexes **1**, **2**, and **3** showed, interestingly, to carry out the catalytic transesterification of a range of esters with methanol at room temperature under the mild conditions, though all these compounds are saturated with two bispicam ligands [26]. To explain this unexpected reactivity, it has been proposed that the hydrogen atom of amine N–H moiety in the complexes could do the acid-catalyzed transesterification.

To further investigate anion effects on geometrical isomerism in this type of complexes and on construction of a variety of Zn^{II} complexes containing chelating ligands, Hdpa and bispicam, and to find efficient catalysts to mediate various catalytic reactions that could be carried out under mild reaction conditions, three more anions (NO_3^-, $C_6H_5CO_2^-$ (benzoate), and OTf^-) have been applied to this

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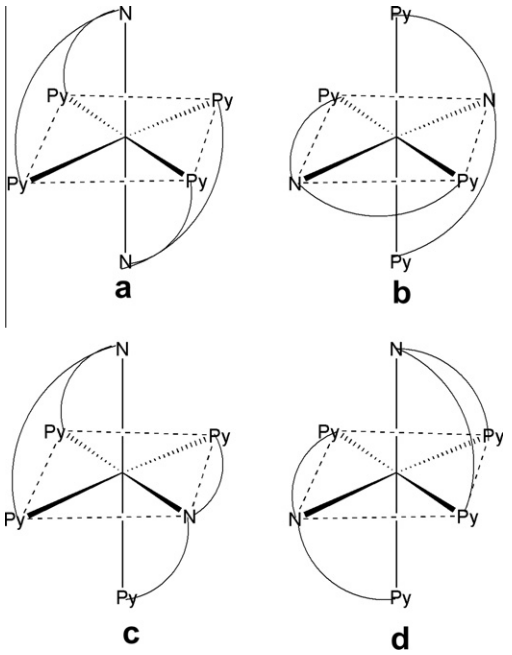


Scheme 1. Potential geometric isomers for the $[Zn(bispicam)_2]^{2+}$ cation.

system. Herein we report the syntheses and crystal structures of three Zn-containing compounds, $[Zn(bispicam)_2](NO_3)_2{\cdot}2CH_3OH$ **4A**, $[Zn(bispicam)(NO_3)_2]$ **4B**, and $[Zn(bispicam)_2](OTf)_2$ **6**, and their catalytic activities including $[Zn(bispicam)_2](ClO_4)_2$ **5** [25] are discussed.

2. Experimental section

2.1. Materials

Methanol, methylene chloride, *para*-substituted phenyl acetate, *para*-substituted phenyl benzoate, methylacetate, methylbenzoate, bis(2-pyridylmethyl)amine, zinc nitrate, $Zn(OTf)_2$, ammonium benzoate, and zinc perchlorate 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, South 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. Syntheses of $[Zn(bispicam)_2](NO_3)_2{\cdot}2CH_3OH$ (**4A**)

$Zn(NO_3)_2$ (37.9 mg, 0.125 mmol) and ammonium benzoate (35.5 mg, 0.25 mmol) were dissolved in 4 mL water and carefully layered by 4 mL methanol solution of bispicam (46.4 mg, 0.25 mmol). Suitable crystals of compound **4A** for X-ray analysis were obtained in a few weeks. The yield was 16.1 mg (20.3%). ^{1}H NMR (DMSO, 300 MHz): δ 7.42–8.55 (m, 16H, aromatic-H), δ 4.80–5.00 (br, 2H, N–H), and δ 4.13 (s, 8H, CH_2). IR (KBr): $\nu(cm^{-1})$ = 3459(brs, H_2O), 3149(brs, N–H), 2923(m), 2349(m), 1605(s), 1574(m), 1488(s), 1439(s), 1355(w), 1315(w), 1283(m), 1242(w), 1158(w), 1086(s), 1054(m), 1013(s), 915(m), 765(s), 730(w), 639(m), 530(brw), 414(m). *Anal.* Calc. for $C_{26}H_{34}N_8O_8Zn$ (651.98), **4A**: C, 47.89; H, 5.27; N, 17.19. Found: C, 48.11; H, 4.98; N, 16.85%.

2.4. Syntheses of $[Zn(bispicam)(NO_3)_2]$ (**4B**)

$Zn(NO_3)_2$ (37.9 mg, 0.125 mmol) was dissolved in 4 mL water and carefully layered by 4 mL methanol solution of bispicam (46.4 mg, 0.25 mmol). Suitable crystals of compound **4B** for X-ray analysis were obtained in a few weeks. The yield was 15.5 mg (21.0%). ^{1}H NMR (DMSO, 300 MHz): δ 7.41–8.61 (m, 8H, aromatic-H), δ 4.20–4.40 (br, 1H, N–H), and δ 4.00 (s, 4H, CH_2). IR

Table 1
Crystallographic data for compounds **4**–**6**.

	4A	**4B**	**5**[a]	**6**
Empirical formula	$C_{26}H_{34}N_8O_8Zn$	$C_{12}H_{12}N_5O_6Zn$	$C_{24}H_{26}Cl_2N_6O_8Zn$	$C_{26}H_{26}F_6N_6O_6S_2Zn$
Formula weight	651.98	387.64	662.78	762.02
Temperature (K)	293(2)	293(2)	293(2)	293(2)
Crystal system	triclinic	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P21/n$	$C2/c$	$P21/c$
a (Å)	9.1790(18)	7.7048(18)	23.695(3)	20.811(4)
b (Å)	9.3570(19)	13.167(3)	9.0073(12)	13.114(2)
c (Å)	9.968(2)	14.905(3)	26.057(3)	18.858(3)
α (°)	84.47(3)	90.00	90.00	90.00
β (°)	72.15(3)	100.221(4)	91.579(2)	113.769(3)
γ (°)	70.89(3)	90.00	90.00	90.00
Volume (Å^3)	770.0(3)	1488.0(6)	5559.4(13)	4710.1(14)
Z	1	4	8	6
Absorption coefficient (mm^{-1})	0.857	1.693	1.135	1.001
Number of data collected	4300	7924	17251	25313
Number of unique data	2949	2915	6572	9115
$R_{(int)}$	0.0850	0.0846	0.0684	0.0892
Goodness-of-fit	1.014	0.828	1.020	0.785
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0632, wR_2 = 0.1648	R_1 = 0.0398, wR_2 = 0.0831	R_1 = 0.0606, wR_2 = 0.1401	R_1 = 0.0733, wR_2 = 0.1597
Final R indices (all data)	R_1 = 0.0735, wR_2 = 0.1692	R_1 = 0.0843, wR_2 = 0.0871	R_1 = 0.1348, wR_2 = 0.1665	R_1 = 0.1595, wR_2 = 0.1783

[a] The crystal structure of **5** was re-determined, and all the parameters were same with the results reported by Glerup et al. [25].

(KBr): $\nu(cm^{-1})$ = 3399(brs, H_2O), 3170(brs, N–H), 2927(m), 2369(m), 1604(s), 1573(m), 1487(s), 1441(s), 1358(w), 1318(w), 1284(m), 1246(w), 1159(w), 1086(s), 1053(m), 1012(s), 915(m), 765(s), 729(w), 639(m), 553(brw), 413(m). *Anal.* Calc. for $C_{12}H_{12}N_5O_6Zn$ (387.64), **4B**: C, 37.18; H, 3.13; N, 18.07. Found: C, 37.53; H, 3.21; N, 17.70%.

2.5. Synthesis of $[Zn(bispicam)_2](OTf)_2$ (**6**)

$Zn(Otf)_2$ (29.7 mg, 0.08 mmol) were dissolved in 4 mL water and carefully layered by 4 mL methanol solution of bispicam (29.7 mg, 0.16 mmol). Suitable crystals of compound **6** for X-ray analysis were obtained in a few weeks. The yield was 16.1 mg (20.3%). ^1H NMR (DMSO, 300 MHz): δ 7.42–8.55 (m, 16H, aromatic-H), δ 4.80–5.00 (br, 2H, N–H), and δ 4.13 (s, 8H, CH_2). IR (KBr): $\nu(cm^{-1})$ = 3459(brs, H_2O), 3149(brs, N–H), 2923(m), 2349(m), 1605(s), 1574(m), 1488(s), 1439(s), 1355(w), 1315(w), 1283(m), 1242(w), 1158(w), 1086(s), 1054(m), 1013(s), 915(m), 765(s), 730(w), 639(m), 530(brw), 414(m). *Anal.* Calc. for $C_{26}H_{26}F_6N_6O_6S_2Zn$ (762.02), **6**: C, 40.98; H, 3.45; N, 11.03. Found: C, 41.32; H, 3.40; N, 11.39%.

2.6. Catalytic activity of compounds **4–6**

Catalytic reaction conditions: Ester (0.05 mmol) was dissolved in methanol (1 mL), and the compounds 4–6 (1.0 mg, 1.28×10^{-3} mmol for **4A**, 1.0 mg, 1.56×10^{-3} mmol for **4B**, 1.0 mg, 1.28×10^{-3} mmol for **5**, and 1.0 mg, 1.44×10^{-3} mmol for **6**) were added and shaken 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. Yields were based on the formation of the products, methylacetate or methylbenzoate.

2.7. X-ray crystallography

The X-ray diffraction data for all four compounds were collected on a Bruker SMART APEX diffractometer equipped with a monochromater 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 V6.10 [27]. All hydrogen atoms were placed in the calculated positions. OTf^- anions are highly disordered in 6. The crystallographic data for compounds **4–6** are listed in Table 1.

3. Results and discussion

In our previous study, we obtained three $[Zn(bispicam)_2]^{2+}$ cations containing free halides with *fac* geometry type (a) in Scheme 1) and concluded that hydrogen bonding interactions between N_{amine}–H and C–H of $[Zn(bispicam)_2]^{2+}$ cations and free halides, and between O_{water}–H and free halides can play very important roles for construction of molecular packing and crystal structures [26]. To investigate anion effects on structures of $[Zn(bispicam)_2]X_2$ complexes, three more anions (NO_3^-, OTf^-, and benzoate) were applied to this system. Complexes of the general formulation $[Zn(bispicam)_2]X_2$ with different anions are shown in Scheme 2.

3.1. Structure description

In 4A, ammonium benzoate was applied to the reaction of $Zn(NO_3)_2$ and bispicam, but benzoate ligands did not coordinate

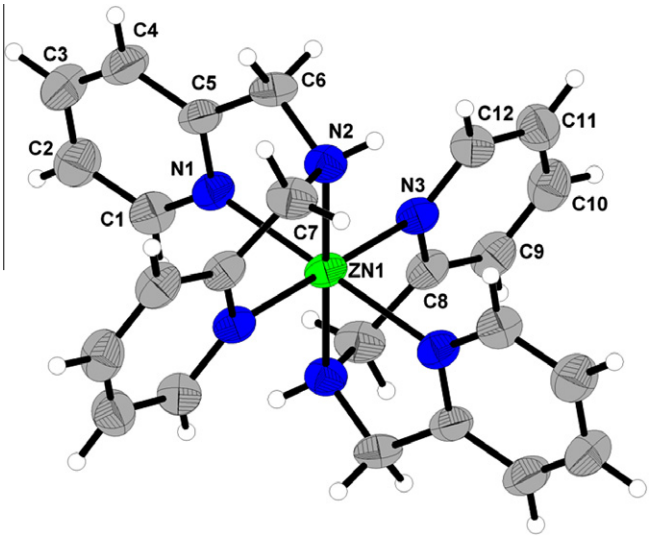
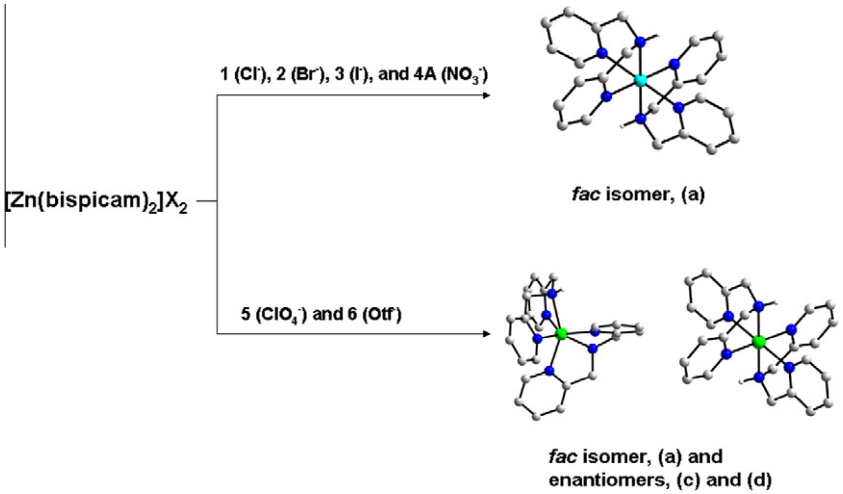


Fig. 1. Structure of $[Zn(bispicam)_2]^{2+}$ in **4A**.



Scheme 2. Anion effects on construction of $[Zn(bispicam)_2]X_2$ complexes.

to the Zn^{II} ion, and instead, two bispicam ligands coordinated to a Zn^{II} ion producing **4A** complex. Asymmetric unit contains half of a molecule, a nitrate anion, and a methanol solvent molecule, and there is an inversion center on a Zn atom. The structure of the whole molecule $[Zn(bispicam)_2](NO_3)_2{\cdot}2CH_3OH$ is shown in Fig. 1. The coordination geometry around a zinc atom is pseudo-octahedral, and the isomer isolated is the *fac* isomer represented (a) above. The Zn–N_{amine} bond distance of 2.160(3) Å is shorter than two Zn–$N_{pyridyl}$ bonds of 2.188(3) and 2.200(3) Å (Table 2). If ammonium benzoate did not applied to this reaction, two nitrate anions coordinate to the Zn ion providing **4B** complex (Fig. 2). The coordination geometry around a zinc atom is distorted trigonal bipyramidal (TBP). The N_{amine} is disordered in two nitrogen atoms with 75 and 25% occupancies. The principle bond distances and angles of **4B** are listed in Table 2.

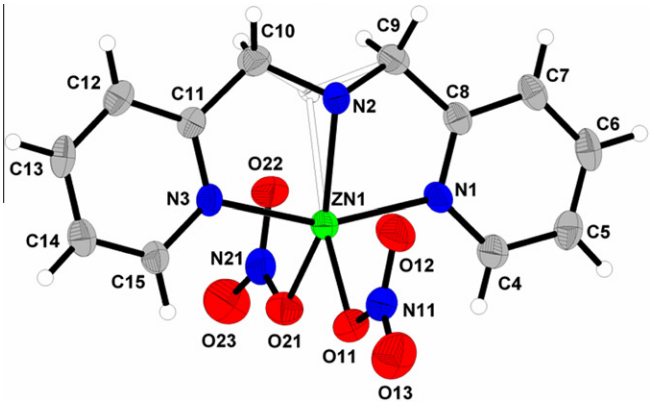


Fig. 2. Structure of $[Zn(bispicam)_2(NO_3)_2]$ **4B**. The open atom represents disordered N2* atom.

There are two crystallographically independent Zn^{II} ions in both **5** [25] and **6**. Zn(1) atom lies on a site of C_2 symmetry providing enantiomers, and Zn(2) atom lies on an inversion center with C_i symmetry (Fig. 3). Fig. 4 shows packing diagrams containing *fac* isomer, (a) and enantiomers, (c) and (d) in a unit cell in both **5** and **6** complexes. According to the centrosymmetric space group, there is an equal distribution of the two enantiomers, (c) and (d). The principle bond distances and angles of **6** are listed in Table 2.

When bispicam ligands react with various Zn^{II} salts (Cl^- (**1**) [25], Br^- (**2**), I^- (**3**) [26], NO_3^- (**4A**), ClO_4^- (**5**) [25] and OTf^- (**6**)),

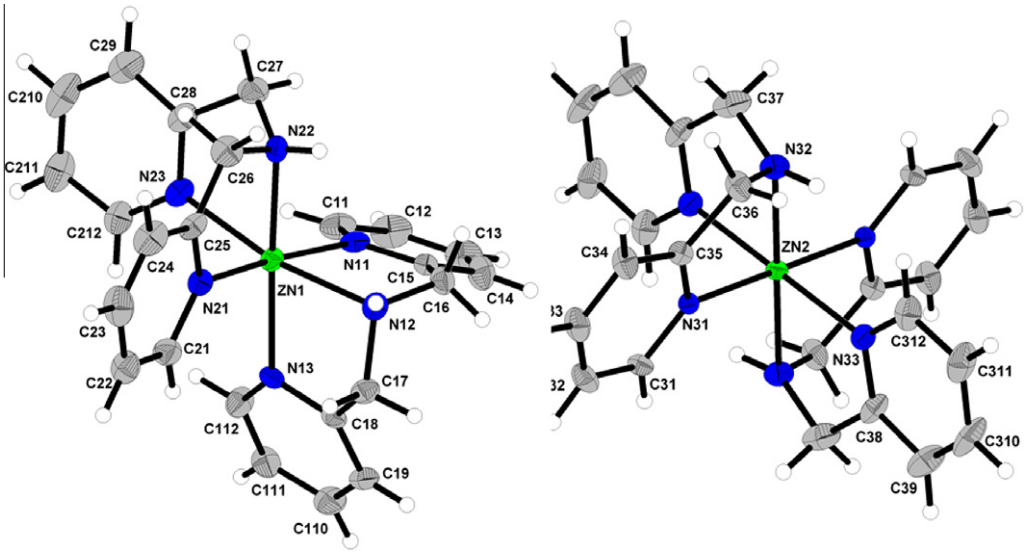


Fig. 3. Structure of $[Zn(bispicam)_2]^{2+}$ in **6** containing two independent isomers.

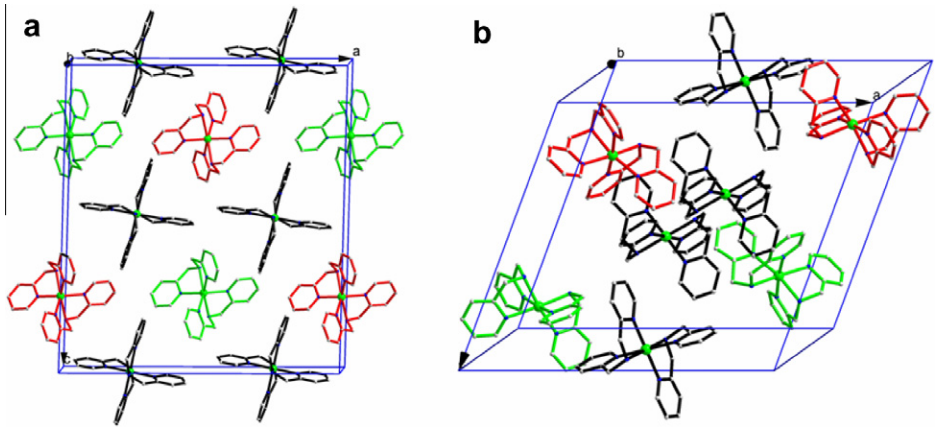


Fig. 4. Packing diagrams in a unit cell with *fac* isomers containing enantiomers representing (a) in black and (c) and (d) in red and blue for **5** (a) and for **6** (b). All ClO_4^- and OTf^- anions, and all hydrogen atoms were omitted for clarity. (For interpretation of the references in color in this figure legend, the reader is referred to the web version of this article.)

complexes of the general formulation $[Zn(bispicam)_2]X_2$ have been obtained, and there were *fac* geometric isomers (a) or enantiomers (c) and (d) according to anions. With halides, $[Zn(bispicam)_2]^{2+}$ cations have only *fac* geometric isomer (a). With coordinating NO_3^- anion, a nitrate-coordinated Zn^{II} complex of the formulation $[Zn(bispicam)(NO_3)_2]$ was obtained. On the other hand, when the benzoate was applied with $Zn(NO_3)_2$, typical $[Zn(bispicam)_2]^{2+}$ cation was obtained and showed *fac* geometric isomer (a). With non-coordinating ClO_4^- and OTf^- anions, there were *fac* isomers (a) and enantiomers (c) and (d) which are, of course, equal distribution of these two enantiomers because of the centrosymmetric space group. These results indicate that anion effects play very important roles for construction of crystal structures and geometrical isomerism. In addition, it is worthwhile to note that, with bispicam ligand, only one structure of the general formulation $[Zn(bispicam)_2]X_2$ (Cl^-, Br^-, I^-, NO_3^-, ClO_4^-, and OTf^-) was obtained except the nitrate-coordinated complex of the formulation $[Zn(bispicam)(NO_3)_2]$, while with Hdpa ligand, various structures (tetrahedral, flattened tetrahedral, six-coordinated mononuclear complexes and a polymeric compound) were observed according to the change of the anions.

3.2. Catalytic transesterification reactions by the compounds **4–6**

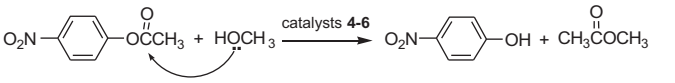
The most common procedure for transesterification reaction is to reflux the ester with a catalytic amount of $Ti(O\text{-}i\text{-}Pr)_4$ in an alcohol solvent [28], while the transesterification reaction is important in organic synthesis in industrial as well as in academic laboratories [29–31]. Other Lewis acid catalysts such as $BuSn(OH)_3$ and $Al(OR)_3$ are also effective for this conversion [32,33], but require higher reaction temperature and acidic conditions. These drawbacks drive us to develop new catalysts that operate under milder conditions. Therefore, with a need for new transesterification catalysts, we have previously reported that $Zn(Hdpa)X_2$ ($X = NO_3^-$, SO_4^{2-}, $^-O_2C_6H_5$, Cl^-, Br^-, and I^-) could carry out the catalytic transesterification of a range of esters with methanol at room temperature under the mild conditions [23,24]. Interestingly, the complexes with labile ligands showed efficient catalytic reactivity, while the complexes with inert ligands or with saturated structures catalyzed slow conversions for transesterification reactions. In addition, we have recently shown that the polymeric compounds $[Zn(bispicam)_2]Cl_2$ **1**, $[Zn(bispicam)_2]Br_2$ **2** and $[Zn(bispicam)_2]I_2$ **3** with non-classical C/N–H···X hydrogen bonding, interestingly, showed

Table 2
Selected bond lengths [Å] and angles [°] for compounds **4A**, **4B**, and **6**.

4A			
Zn(1)–N(2)	2.160(3)	Zn(1)–N(2)#1	2.160(3)
Zn(1)–N(3)#1	2.188(3)	Zn(1)–N(3)	2.188(3)
Zn(1)–N(1)#1	2.200(3)	Zn(1)–N(1)	2.200(3)
N(2)–Zn(1)–N(2)#1	180.0	N(2)–Zn(1)–N(3)#1	79.65(12)
N(2)#1–Zn(1)–N(3)#1	100.35(12)	N(2)–Zn(1)–N(3)	100.35(12)
N(2)#1–Zn(1)–N(3)	79.65(12)	N(3)#1–Zn(1)–N(3)	180.0
N(2)–Zn(1)–N(1)#1	100.24(13)	N(2)#1–Zn(1)–N(1)#1	79.76(13)
N(3)#1–Zn(1)–N(1)#1	93.03(12)	N(3)–Zn(1)–N(1)#1	86.97(12)
N(2)–Zn(1)–N(1)	79.76(13)	N(2)#1–Zn(1)–N(1)	100.24(13)
N(3)#1–Zn(1)–N(1)	86.97(12)	N(3)–Zn(1)–N(1)	93.03(12)
N(1)#1–Zn(1)–N(1)	180.00		
Symmetry transformations used to generate equivalent atoms: #1 $-x+1$, $-y+1$, $-z+1$			
4B			
Zn(1)–O(11)	2.071(3)	Zn(1)–N(1)	2.090(3)
Zn(1)–O(21)	2.094(3)	Zn(1)–N(3)	2.100(3)
Zn(1)–N(2)	2.160(5)	Zn(1)–N(2*)	2.243(14)
O(11)–Zn(1)–N(1)	101.31(12)	O(11)–Zn(1)–O(21)	85.52(14)
N(1)–Zn(1)–O(21)	99.36(12)	O(11)–Zn(1)–N(3)	97.47(12)
N(1)–Zn(1)–N(3)	156.49(12)	O(21)–Zn(1)–N(3)	96.07(11)
O(11)–Zn(1)–N(2)	127.4(3)	N(1)–Zn(1)–N(2)	79.07(15)
O(21)–Zn(1)–N(2)	146.9(3)	N(3)–Zn(1)–N(2)	78.32(15)
O(11)–Zn(1)–N(2*)	156.1(7)	N(1)–Zn(1)–N(2*)	79.7(3)
O(21)–Zn(1)–N(2*)	118.1(8)	N(3)–Zn(1)–N(2*)	77.4(3)
N(2)–Zn(1)–N(2*)	28.9(5)		
6			
Zn(1)–N(21)	2.091(6)	Zn(1)–N(11)	2.150(6)
Zn(1)–N(22)	2.159(6)	Zn(1)–N(12)	2.170(6)
Zn(1)–N(13)	2.224(5)	Zn(1)–N(23)	2.226(6)
Zn(2)–N(33)#1	2.150(5)	Zn(2)–N(33)	2.151(6)
Zn(2)–N(32)	2.153(6)	Zn(2)–N(32)#1	2.153(6)
Zn(2)–N(31)#1	2.180(5)	Zn(2)–N(31)	2.180(5)
N(21)–Zn(1)–N(11)	174.1(2)	N(21)–Zn(1)–N(22)	80.4(2)
N(11)–Zn(1)–N(22)	100.6(2)	N(21)–Zn(1)–N(12)	95.3(2)
N(11)–Zn(1)–N(12)	78.9(2)	N(22)–Zn(1)–N(12)	96.4(2)
N(21)–Zn(1)–N(13)	97.2(2)	N(11)–Zn(1)–N(13)	81.2(2)
N(22)–Zn(1)–N(13)	175.1(2)	N(12)–Zn(1)–N(13)	79.5(2)
N(21)–Zn(1)–N(23)	91.3(2)	N(11)–Zn(1)–N(23)	94.5(2)
N(22)–Zn(1)–N(23)	76.8(2)	N(12)–Zn(1)–N(23)	169.6(2)
N(13)–Zn(1)–N(23)	107.7(2)	N(33)#1–Zn(2)–N(33)	180.0
N(33)#1–Zn(2)–N(32)	80.2(2)	N(33)–Zn(2)–N(32)	99.8(2)
N(33)#1–Zn(2)–N(32)#1	99.8(2)	N(33)–Zn(2)–N(32)#1	80.2(2)
N(32)–Zn(2)–N(32)#1	180.0	N(33)#1–Zn(2)–N(31)#1	90.49(19)
N(33)–Zn(2)–N(31)#1	89.51(19)	N(32)–Zn(2)–N(31)#1	100.2(2)
N(32)#1–Zn(2)–N(31)#1	79.8(2)	N(33)#1–Zn(2)–N(31)	89.51(19)
N(33)–Zn(2)–N(31)	90.49(19)	N(32)–Zn(2)–N(31)	79.8(2)
N(32)#1–Zn(2)–N(31)	100.2(2)	N(31)#1–Zn(2)-N(31)	180.0
Symmetry transformations used to generate equivalent atoms: #1 $-x+1$, $-y+1$, $-z$			

to carry out the catalytic transesterification of a range of esters with methanol at room temperature under the mild conditions, though all these compounds are saturated with two bispicam ligands. To explain this unexpected reactivity, it has been proposed that the hydrogen atom of amine N-H moiety in the complexes could do the acid-catalyzed transesterification.

Therefore, in order to compare the reactivity of the complex **4B** having the unsaturated structure to those of the complexes **4A**, **5**, and **6** having the saturated structures, we have examined the transesterification reaction with the compounds **4**–**6**. Thus, the compounds **4**–**6** were treated with 4-nitrophenyl acetate and methanol at 50 °C under the neutral conditions.



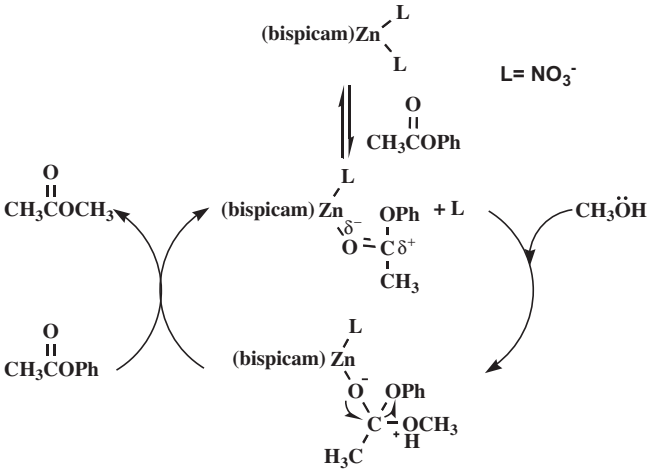
(1)

This reaction produced quantitatively the corresponding product methyl acetate within 0.25–0.54 days (entry 1 of Table 3), while a control reaction carried out in absence of the complexes showed trace amounts of the conversion of the ester to the product in the same time period. Importantly, the transesterification reactivity shown by the catalyst **4B** is very efficient and the second best among the catalytic efficiencies reported previously with Zn-containing compounds, to our best knowledge [34–39].

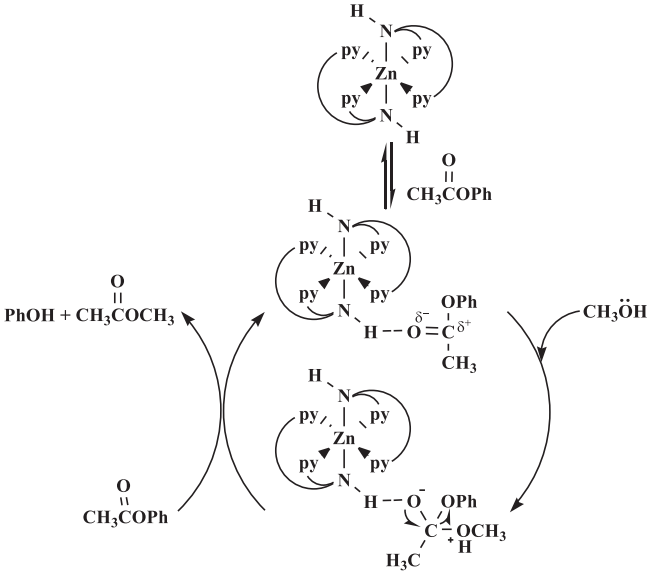
The transesterification of other esters including benzoates by the catalysts **4**–**6** was also carried out efficiently and the results are given in Table 3. The substrates with the electron-withdrawing substituents have undergone faster transesterification, while those with the electron-donating ones have shown slow reaction. Importantly, vinyl acetate, which is widely used as a precursor for ester synthesis [40,41], was also converted efficiently to the product methyl acetate within 0.13–0.21 days by the catalysts (entry 8), suggesting that this catalytic system can be useful for preparing various esters by transesterification. It is worthwhile to note that the catalysts **4B** with an unsaturated structure have shown better efficiency than the catalysts, **1**, **2**, **3**, **4A**, **5**, and **6**, having saturated structures, as also previously shown in zinc complexes with Hdpa ligand [23,24].

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 are able to propose two possible transesterification reaction mechanisms based on the structure of the complexes **4**–**6** and our pervious results [24]. With **4B** having the labile ligand NO_3^-, the plausible mechanism is shown in Scheme 3. The substrate phenyl acetate substitutes an anion (NO_3^-) to give the adduct $(bispicam)_2Zn(NO_3)(Sub)$. Then, the nucleophile methanol would attack the carbon atom of carbonyl moiety of the adduct to produce the product methyl acetate.

With complexes, **4A**, **5**, and **6**, having the saturated structures, we can presume that there is no direct interaction between the substrate ester and zinc ion of the complexes as Lewis acid, since they all are saturated with two bispicam ligands. Therefore, we propose that the hydrogen atom of amine N–H moiety in the complexes can do the acid-catalyzed transesterification as previously proposed [23], because the hydrogen atom could be acidic by coordinating of nitrogen of N–H to zinc ion (Scheme 4). Thus, this acidic hydrogen interacts with the oxygen atom of carbonyl of ester, resulting in that the carbonyl is more electrophilic. Then, the resultant activated carbonyl could be easily attacked by



Scheme 3. Proposed reaction mechanism with the unsaturated complex 4B.



Scheme 4. Proposed reaction mechanism with the saturated complexes **4A**, **5**, and **6**.

Table 3
Transesterification of esters by methanol in the presence of compounds **4**–**6** at 50 °C. [a].

Entry	Substrate	**4A** (time/days) [b]	**4B** (time/days) [b]	**5** (time/days) [b]	**6** (time/days) [b]
1	4-Nitrophenyl acetate	0.54	0.25	0.38	0.31
2	Phenyl acetate	4	0.92	2	2
3	4-Methylphenyl acetate	3	2	3	3
4	4-Nitrophenyl benzoate [c]	9	7	5	7
5	4-Chlorophenyl benzoate	2	0.71	3	2
6	Phenyl benzoate	4	1.63	4	2
7	4-Methylphenyl benzoate	2	0.75	4	3
8	Vinyl acetate	0.16	0.13	0.17	0.21

[a] All esters were completely converted to the corresponding products, methyl acetate and methyl benzoate. Reaction conditions: esters; 0.05 mmol, catalyst; 1.28×10^{-3} mmol for **4A**, 1.56×10^{-3} mmol for **4B**, 1.44×10^{-3} mmol for **5**, and 1.44×10^{-3} mmol for **6**, solvent; methanol (1 mL). See the experimental section 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.

methanol to produce the product methyl ester as shown in Scheme 4.

4. Conclusions

Complexes of the general formulation $[Zn(bispicam)_2]X_2$ ($X = Cl^-$ [25], Br^-, I^- [26], NO_3^-, ClO_4^- [25], and OTf^-) have been obtained, and there were *fac* geometric isomers (a) or enantiomers (c) and (d) according to anions. These results indicate that anion effects play very important roles for construction of crystal structures and geometrical isomerism. We have also reported that complexes **4**–**6**, could carry out the catalytic transesterification of a range of esters with methanol under the mild conditions. Interestingly, the catalyst **4B** with an unsaturated structure has shown better efficiency than the catalysts, **4A**, **5**, and **6**, having saturated structures. To explain this reactivity difference, two different reaction mechanisms have been proposed (metal-based *vs*. amide N–H based). These results may represent an excellent starting point for the development of new metal complexes that might be efficiently used as useful catalysts.

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Appendix A. Supplementary material

CCDC 764846, 764847 and 764848 contain the supplementary crystallographic data for compounds **4A**, **4B** and **6**, 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 doi:10.1016/j.ica.2010.11.029.

References

[1] D.B. Moler, H. Li, B. Chen, T.M. Reineke, M. O'Keeffe, O.M. Yaghi, Acc. Chem. Res. 34 (2001) 319.
[2] B. Moulton, M.J. Zaworotko, Chem. Rev. 101 (2001) 1629.
[3] O.R. Evans, W. Lin, Acc. Chem. Res. 35 (2002) 511.
[4] A. Erxleben, Coord. Chem. Rev. 246 (2003) 203.
[5] S.A. Barnett, N.R. Champness, Coord. Chem. Rev. 246 (2003) 145.
[6] L. Carlucci, G. Ciani, D.M. Proserpio, Coord. Chem. Rev. 246 (2003) 247.
[7] H.W. Roesky, M. Andruh, Coord. Chem. Rev. 236 (2003) 91.
[8] X.J. Luan, Y.-Y. Wang, D.-S. Li, P. Liu, H.-M. Hu, Q.-Z. Shi, S.-M. Peng, Angew. Chem., Int. Ed. 44 (2005) 3864.
[9] B.-B. Ding, Y.-Q. Weng, Z.-W. Mao, C.-K. Lam, X.-M. Chen, B.-H. Ye, Inorg. Chem. 44 (2005) 8836.
[10] A. Angeloni, P.C. Crawford, A.G. Orpen, T.J. Podesta, B.J. Shore, Chem. Eur. J. 10 (2004) 3783.
[11] V. Balamurugan, M.S. Hundal, R. Mukherjee, Chem. Eur. J. 10 (2004) 1683.
[12] Y. Wang, J. Yu, Y. Li, Z. Shi, R. Xu, Chem. Eur. J. 9 (2003) 5048.
[13] D. Braga, F. Grepioni, G.R. Desiraju, Chem. Rev. 98 (1998) 1375.
[14] C. Janiak, Dalton Trans. (2003) 2781.
[15] L. Carlucci, G. Ciani, D.M. Proserpio, S. Rizzato, Chem. Eur. J. 5 (1999) 237.
[16] H.-P. Wu, C. Janiak, G. Rheinwald, H. Lang, J. Chem. Soc. (1999) 183.
[17] Z. Ni, J. Vittal, Cryst. Growth Des. 1 (2001) 195.
[18] M. Du, X.-H. Bu, Y.-M. Guo, H. Liu, S.R. Batten, J. Ribas, T.C.W. Mak, Inorg. Chem. 41 (2002) 4904.
[19] 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 358 (2005) 3659.
[20] A.J. Blake, N.R. Champness, P. Hubberstey, W.-S. Li, M.A. Withersby, M. Schröder, Coord. Chem. Rev. 183 (1999) 117.
[21] M.C. Hong, Y.J. Zhao, W.P. Su, R. Cao, M. Fujita, Z.Y. Zhou, A.S.C. Chan, J. Am. Chem. Soc. 122 (2000) 4819.
[22] J.F. Ma, J.F. Liu, X. Yan, H.Q. Jia, Y.H. Lin, J. Chem. Soc. (2000) 2403.
[23] Y.M. Lee, S.J. Hong, H.J. Kim, S.H. Lee, H. Kwak, C. Kim, S.-J. Kim, Y. Kim, Inrog. Chem. Commun. 10 (2007) 287.
[24] H. Kwak, S.H. Lee, S.H. Kim, Y.M. Lee, E.Y. Lee, B.K. Park, E.Y. Kim, C. Kim, S.-J. Kim, Y. Kim, Eur. J. Inorg. Chem. (2008) 408.
[25] J. Glerup, P.A. Goodson, D.J. Hodgson, K. Michelsen, K.M. Nielsen, H. Welbe, Inorg. Chem. 31 (1992) 4611.
[26] B.K. Park, S.H. Lee, E.Y. Lee, H. Kwak, Y.M. Lee, Y.J. Lee, J.Y. Jun, C. Kim, S.-J. Kim, Y. Kim, J. Mol. Struct. 890 (2008) 123.
[27] Bruker, SHELXTL/PC, Version 6.12 for Windows XP. 2001, Bruker AXS Inc., Madison, Wisconsin, USA.
[28] D. Seebach, E. Hungerbuhler, R. Naef, D. Schnurrenberger, B. Weidmann, M. Zuger, Synthesis (1982) 138.
[29] M.-H. Lin, T.V. RajanBabu, Org. Lett. 2 (2000) 997.
[30] G.A. Grasa, R.M. Kissling, S.P. Nolan, Org. Lett. 4 (2002) 3583.
[31] G.A. Grasa, T. Guveli, R. Singh, S.P. Nolan, J. Org. Chem. 68 (2003) 2812.
[32] R.L.E. Furlan, E.G. Mata, O.A. Mascaretti, Tetrahedron Lett. 39 (1998) 2257.
[33] C.E. Rehberg, C.H. Fisher, J. Org. Chem. 12 (1947) 226.
[34] 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 359 (2006) 2534.
[35] J.Y. Kwon, Y. Kim, S.-J. Kim, S.H. Lee, H. Kwak, C. Kim, Inorg. Chim. Acta 361 (2008) 1885.
[36] L. Xu, Y. Kim, S.-J. Kim, H.J. Kim, C. Kim, Inrog. Chem. Commun. 10 (2007) 586.
[37] Y.J. Song, H. Kwak, Y.M. Lee, S.H. Kim, S.H. Lee, B.K. Park, J.Y. Jun, S.M. Yu, C. Kim, S.-J. Kim, Y. Kim, Polyhedron 28 (2009) 1241.
[38] S.H. Kim, B.K. Park, Y.J. Song, S.M. Yu, H.G. Koo, E.Y. Kim, J.I. Poong, J.H. Lee, C. Kim, S.-J. Kim, Y. Kim, Inorg. Chim. Acta 362 (2009) 4119.
[39] H. Kwak, S.H. Lee, S.H. Kim, Y.M. Lee, B.K. Park, Y.J. Lee, J.Y. Jun, C. Kim, S.-J. Kim, Y. Kim, Polyhedron 28 (2009) 553.
[40] G.W. Nyce, J.A. Lamboy, E.F. Connor, R.M. Waymouth, J.L. Hedrick, Org. Lett. 4 (2002) 3587.
[41] D. Tashiro, Y. Kawasaki, S. Sakaguchi, Y. Ishii, J. Org. Chem. 62 (1997) 8141.