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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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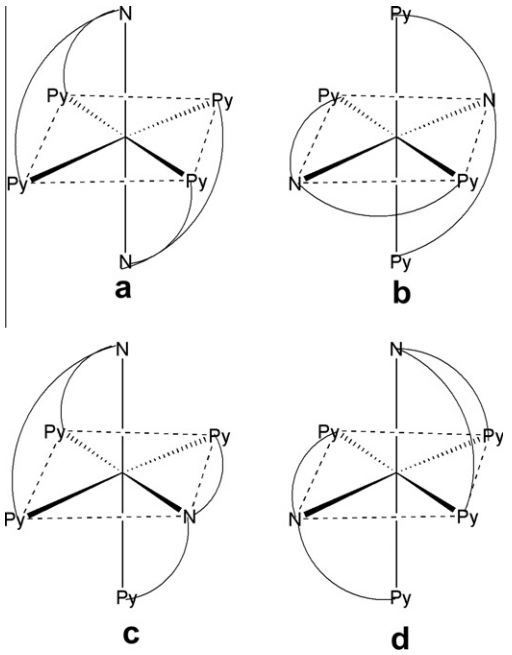

Scheme 1. Potential geometric isomers for the $[Zn(bispicam)_2]^{2+}$ cation.

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].