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Zinc(II) polymeric compounds with a chelating ligand bis(2-pyridylmethyl)amine (bispicam) directed by intermolecular C/N/O–H···X (X = Cl, Br, I) interactions: Catalytic activities

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ABSTRACT

$[Zn(bispicam)_2]^{2+}$ as a hydrogen-bond donor and three free halides (Cl^-, Br^- and I^-) as hydrogen-bond acceptors were employed to investigate the role of non-classical C/N–H···X hydrogen bonding for construction of polymeric compounds. Three zinc salts ($ZnCl_2$, $ZnBr_2$ and ZnI_2) were reacted with bis(2-pyridylmethyl)amine (bispicam) to produce $[Zn(bispicam)_2]Cl_2$ **1**, $[Zn(bispicam)_2]Br_2$ **2** and $[Zn(bispicam)_2]I_2$ **3**. 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. In addition, these hydrogen-bonded complexes **1**, **2** and **3** were, interestingly, shown to carry out the catalytic transesterification of a range of esters with methanol at 50 °C under the mild conditions, though all these compounds are saturated with two bispicam ligands. To explain this unusual reactivity, it has been proposed that the hydrogen atom of amine N–H moiety in the complexes could do the acid-catalyzed transesterification.

1. Introduction

Classical and non-classical hydrogen bonding provides a good structural motif for construction of a polymeric compound from a simple building block [1]. Much attention has been paid to the role played by non-classical C–H···O/N hydrogen bonding in construction of molecular packing and crystal structures [2]. Weak non-classical C/N–H···X (X = halide) hydrogen bonding can also be a structural motif for construction of polymeric compounds and can stabilize the crystal structures even though they have often been considered as van der Waals interactions, especially when X characters are halide anions or M–X bonds [3,4]. We and others have previously shown that a chelating ligand 2,2′-dipyridylamine (Hdpa) has mostly formed mononuclear Zn(II) complexes by the reaction with zinc salts [5], and then these Zn(II) complexes can be used as building blocks for construction of polymeric compounds through weak non-classical C/N–H···X and C/N–H···O hydrogen bonding [6]. With halide anions among them, especially, the intermolecular N–H···X and C–H···X (X = Cl, Br and I) hydrogen bond interactions played important roles to form a 2-dimensional framework [6]. Moreover, these hydrogen-bonded polymers, $Zn(Hdpa)Cl_2$, $Zn(Hdpa)Br_2$ and $Zn(Hdpa)I_2$, have shown, surprisingly, unusual heterogeneous catalytic activities on transesterification reaction of esters.

Bis(2-pyridylmethyl)amine (bispicam) is another chelating tridentate ligand that is similar to the chelating ligand Hdpa with N–H moiety. Therefore it is expected that the N–H moiety could help construct polymeric compounds through weak non-classical N–H···X hydrogen bonding as shown in $[Zn(Hdpa)X_2]$ complexes (X = Cl^-, Br^- and I^-).

To further investigate the role of non-classical C/N–H···X hydrogen bonding for construction of polymeric compounds and to find efficient catalysts to mediate various catalytic reactions that could be carried out under mild reaction conditions, we have employed $[Zn(bispicam)_2]^{2+}$ as a hydrogen-bond donor and three zinc halides ($ZnCl_2$, $ZnBr_2$ and ZnI_2) as hydrogen-bond acceptors. Herein we report the synthesis, crystal structures and reactivities of three Zn-containing compounds, $[Zn(bispicam)_2]Cl_2$ **1** [7], $[Zn(bispicam)_2]Br_2$ **2** and $[Zn(bispicam)_2]I_2$ **3**, formed by the reaction of the chelating bispicam ligand and three zinc halides.

2. Experimental section

2.1. Materials

Methanol, methylene chloride, *para*-substituted phenyl acetate, *para*-substituted phenyl benzoate, methylacetate, methylbenzoate, bis(2-pyridylmethyl)amine and zinc halides were purchased from

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Aldrich and were used as received. 4-Fluorophenyl acetate and 4-nitrophenyl benzoate were obtained from Lancaster.

2.2. Instrumentation

Elemental analysis for carbon, nitrogen and hydrogen was carried out by using an EA1108 (Carlo Erba Instrument, Italy) in the Organic Chemistry Research Center of Sogang University, Korea. IR spectra were measured on a BIO RAD FTS 135 spectrometer as KBr pellets. Product analysis for the transesterification reaction was performed on either a Hewlett-Packard 5890 II Plus gas chromatograph interfaced with Hewlett-Packard Model 5989B mass spectrometer or a Donam Systems 6200 gas chromatograph equipped with a FID detector using 30-m capillary column (Hewlett-Packard, HP-1, HP-5 and Ultra 2).

2.3. Synthesis of [Zn(bispicam)$_2$]Cl$_2$ (**1**)

A total of 17.38 mg (0.125 mmol) of $ZnCl_2$ were dissolved in 4 mL water and carefully layered by 4 mL methanol solution of bis(2-pyridylmethyl)amine (46.38 μL, 0.25 mmol). Suitable crystals of compound **1** 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, 16H, aromatic-H), δ 4.20–4.40 (br, 2H, N–H), δ 4.00 (s, 8H, CH_2) and δ 3.37 (s, H_2O). IR (KBr): $\nu(\mathrm{cm}^{-1}) = 3399$(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. Calcd. for $C_{24}H_{38}Cl_2N_6O_6Zn$ (642.87), **1**: C, 44.84; H, 5.97; N, 13.08. Found: C, 44.35; H, 6.01; N, 13.36%.

2.4. Synthesis of [Zn(bispicam)$_2$]Br$_2$ (**2**)

A total of 18.38 mg (0.08 mmol) of $ZnBr_2$ were dissolved in 4 mL water and carefully layered by 4 mL methanol solution of bis(2-pyridylmethyl)amine (29.68 mg, 0.16 mmol). Suitable crystals of compound **2** 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), δ 4.13 (s, 8H, CH_2) and δ 3.37 (s, H_2O). IR (KBr): $\nu(\mathrm{cm}^{-1}) = 3459$(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. Calcd. for $C_{24}H_{34}Br_2N_6O_4Zn$ (695.76), **2**: C, 41.43; H, 4.94; N, 12.08. Found: C, 41.52; H, 4.58; N, 12.10%.

2.5. Synthesis of [Zn(bispicam)$_2$]I$_2$ (**3**)

Bis(2-pyridylmethyl)amine (29.68 mg, 0.16 mmol) was dissolved in 4 mL methylene chloride and carefully layered by 4 mL methanol solution of 26.05 mg (0.08 mmol) of ZnI_2. Suitable crystals of compound **3** for X-ray analysis were obtained in a few weeks. The yield was 10.6 mg (11.1%). ^{1}H NMR (DMSO, 300 MHz): δ 7.41–8.44 (m, 16H, aromatic-H), δ 5.48-5.62 (brs, 2H, N–H), δ 4.27 (s, 8H, CH_2) and δ 3.37 (s, H_2O). IR (KBr): $\nu(\mathrm{cm}^{-1}) = 3471$(brs, H_2O), 3116(brs, N–H), 2917(brs), 2362(m), 1605(s), 1573(s), 1486(s), 1438(s), 1354(w), 1314(w), 1283(m), 1249(w), 1154(m), 1089(m), 1054(m), 1014(s), 917(m), 761(s), 729(w), 639(m), 475(w), 413(m). Anal. Calcd. for $C_{26}H_{34}I_2N_6O_2Zn$ (781.76), **3**: C, 39.94; H, 4.39; N, 10.75. Found: C, 40.44; H, 4.12; N, 10.99%.

2.6. Catalytic activity of compounds **1**–**3**

Catalytic reaction conditions: ester (0.05 mmol) was dissolved in an appropriate solvent (1 mL), and the compounds **1**–**3** (1.0 mg, 1.56×10^{-3} mmol for **1**, 1.0 mg, 1.44×10^{-3} mmol for **2** and 1.0 mg, 1.28×10^{-3} mmol for **3**) 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

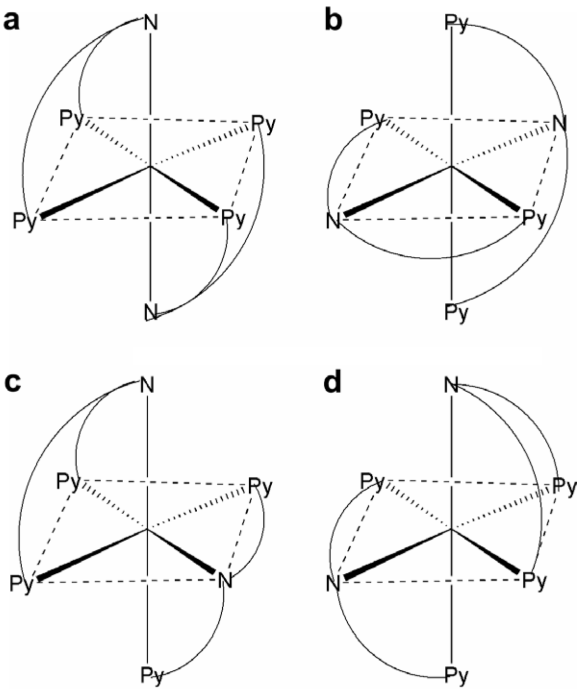
The X-ray diffraction data for all three compounds were collected on a Bruker SMART APX diffractometer equipped with a monochromater in the Mo Kα ($\lambda = 0.71073$ Å) incident beam. Each crystal was mounted on a glass fiber. The CCD data were integrated and scaled using the Bruker-SAINT software package, and the structure was solved and refined using SHEXTL V5.10 [8]. All hydrogen atoms were placed in the calculated positions. The crystallographic data for compounds **1**–**3** are listed in

Table 1
Crystallographic data for compounds **1**–**3**

	1[a]	**2**	**3**
Empirical formula	$C_{24}H_{38}Cl_2N_6O_6Zn$	$C_{24}H_{34}Br_2N_6O_4Zn$	$C_{26}H_{34}I_2N_6O_2Zn$
Formula weight	642.87	695.76	781.76
Temp. (K)	293(2)	293(2)	293(2)
Crystal system	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
a (Å)	9.1805(13)	10.118(2)	9.0649(8)
b (Å)	10.0775(14)	18.560(4)	9.4629(9)
c (Å)	16.448(2)	15.967(3)	9.8747(9)
α (°)	90.00	90.00	76.3630(10)
β (°)	94.553(2)	102.12(3)	82.965(2)
γ (°)	90.00	90.00	68.6040(10)
Volume (Å^3)	1516.9(4)	2931.6(10)	765.82(12)
Z	2	4	1
Absorption coefficient (mm^{-1})	1.032	3.603	2.850
No. of data collected	7540	16,226	4313
No. of unique data	2921	5741	2934
R(int.)	0.0598	0.0380	0.0609
Goodness-of-fit	0.848	1.011	1.080
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0428$, $wR_2 = 0.0982$	$R_1 = 0.0373$, $wR_2 = 0.0758$	$R_1 = 0.0365$, $wR_2 = 0.0953$
Final R indices (all data)	$R_1 = 0.0971$, $wR_2 = 0.1358$	$R_1 = 0.0743$, $wR_2 = 0.0866$	$R_1 = 0.0381$, $wR_2 = 0.0963$

[a] [Zn(bispicam)$_2$]Cl$_2$ **1** was reported previously [7], but we ourselves prepared it again to investigate the role of non-classical C/N–H···X hydrogen bonding for construction of polymeric compounds containing [Zn(bispicam)$_2$]$^{2+}$ units.

Table 1. Structural information was deposited at the Cambridge Crystallographic Data Center (CCDC reference numbers 672358 for **2**, 672359 for **3**).



Scheme 1.

3. Results and discussion

3.1. Synthesis

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). For a 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 [7]. In this study three zinc salts ($ZnCl_2$, $ZnBr_2$ and ZnI_2) were reacted with bispicam to produce $[Zn(bispicam)_2]Cl_2$ **1**, $[Zn(bispicam)_2]Br_2$ **2** and $[Zn(bispicam)_2]I_2$ **3**. Only (a) facial isomers are isolated in our system. $[Zn(bispicam)_2]Cl_2$ **1** was reported previously [7], but we ourselves prepared it again to investigate the role of non-classical C/N–H···X hydrogen bonding for construction of polymeric compounds containing $[Zn(bispicam)_2]^{2+}$ units.

Table 2
Selected bond lengths [Å] and angles [°] for compound **1**

Zn(1)–N(2)#1	2.153(3)	Zn(1)–N(2)	2.153(3)
Zn(1)–N(3)	2.166(3)	Zn(1)–N(3)#1	2.166(3)
Zn(1)–N(1)#1	2.202(4)	Zn(1)–N(1)	2.202(4)
N(2)#1–Zn(1)–N(2)	180.0	N(2)#1–Zn(1)–N(3)	79.76(13)
N(2)–Zn(1)–N(3)	100.25(13)	N(2)#1–Zn(1)–N(3)#1	100.24(13)
N(2)–Zn(1)–N(3)#1	79.75(13)	N(3)–Zn(1)–N(3)#1	180.0
N(2)#1–Zn(1)–N(1)#1	79.94(13)	N(2)–Zn(1)–N(1)#1	100.06(13)
N(3)–Zn(1)–N(1)#1	84.79(12)	N(3)#1–Zn(1)–N(1)#1	95.21(12)
N(2)#1–Zn(1)–N(1)	100.06(13)	N(2)–Zn(1)–N(1)	79.94(13)
N(3)–Zn(1)–N(1)	95.22(12)	N(3)#1–Zn(1)–N(1)	84.79(12)
N(1)#1–Zn(1)–N(1)	180.0		

Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y$, $-z$.

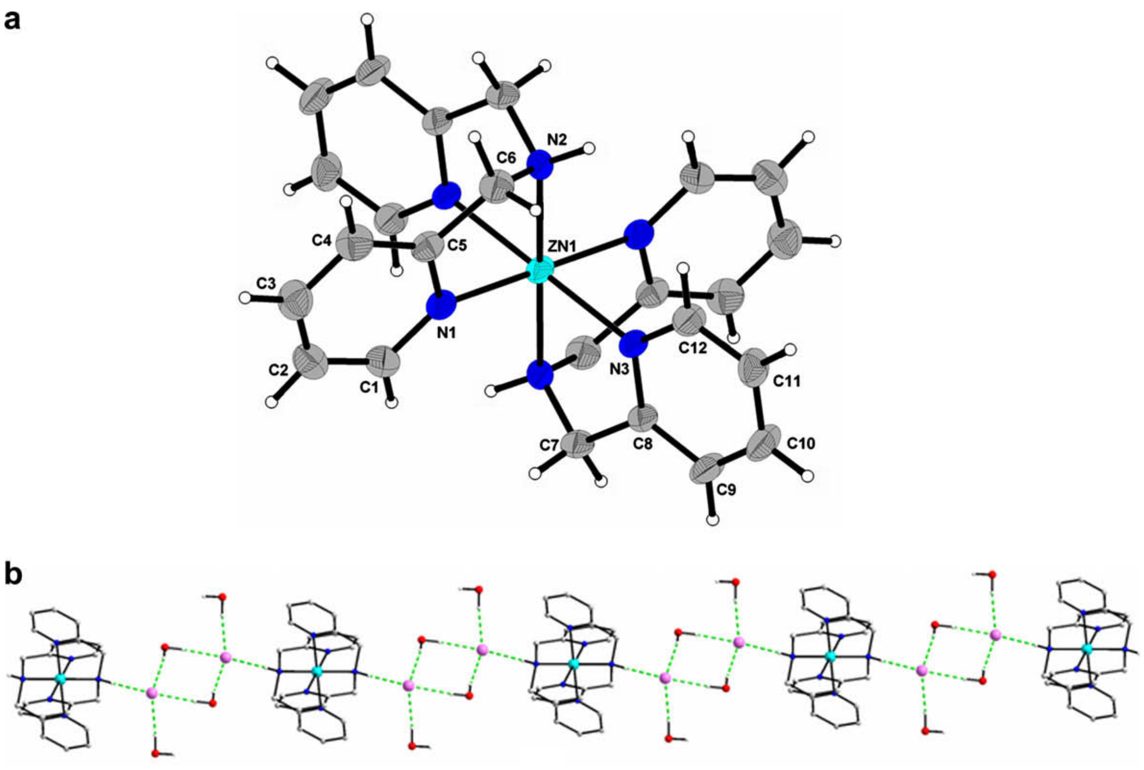


Fig. 1. (a) Structure of the cation of compound **1**. Displacement ellipsoids are shown at the 30% probability level. (b) Hydrogen bond interactions in a one-dimensional polymeric compound. H atoms not involved in intermolecular interactions have been omitted for clarity. Green dotted lines represent N_{amine}–H···Cl and O_{water}–H···Cl hydrogen bonds.

Table 3
Hydrogen bonds for compound **1** (Å and °)

D–H…A	*d*(D–H)	*d*(H…A)	*d*(D…A)	∠(DHA)
N(2)–H(2N)…Cl(1)#2	0.88(4)	2.36(4)	3.234(4)	172(3)
O(2S)–H(2S1)…Cl(1)	0.960(2)	2.228(8)	3.185(5)	174(5)
O(1S)–H(1S2)…Cl(1)#3	0.960(2)	2.26(2)	3.168(4)	157(5)
O(1S)–H(1S1)…Cl(1)#4	0.960(2)	2.291(6)	3.249(4)	175(5)

Symmetry transformations used to generate equivalent atoms: #1 $-x$, $-y$, $-z$; #2 $x-1$, y, $z-1$; #3 x, y, $z-1$; #4 $-x+1$, $-y+1$, $-z+1$.

Table 4
Selected bond lengths [Å] and angles [°] for compound **2**

Zn(1)–N(12)	2.157(3)	Zn(1)–N(13)	2.169(3)
Zn(1)–N(23)	2.174(3)	Zn(1)–N(22)	2.177(3)
Zn(1)–N(11)	2.184(3)	Zn(1)–N(21)	2.192(3)
N(12)–Zn(1)–N(13)	79.62(11)	N(12)–Zn(1)–N(23)	100.13(11)
N(13)–Zn(1)–N(23)	179.69(10)	N(12)–Zn(1)–N(22)	179.57(12)
N(13)–Zn(1)–N(22)	100.57(11)	N(23)–Zn(1)–N(22)	79.68(11)
N(12)–Zn(1)–N(11)	79.67(11)	N(13)–Zn(1)–N(11)	84.16(10)
N(23)–Zn(1)–N(11)	95.98(10)	N(22)–Zn(1)–N(11)	100.73(11)
N(12)–Zn(1)–N(21)	100.71(10)	N(13)–Zn(1)–N(21)	96.25(10)
N(23)–Zn(1)–N(21)	83.61(10)	N(22)–Zn(1)–N(21)	78.89(10)
N(11)–Zn(1)–N(21)	179.48(10)		

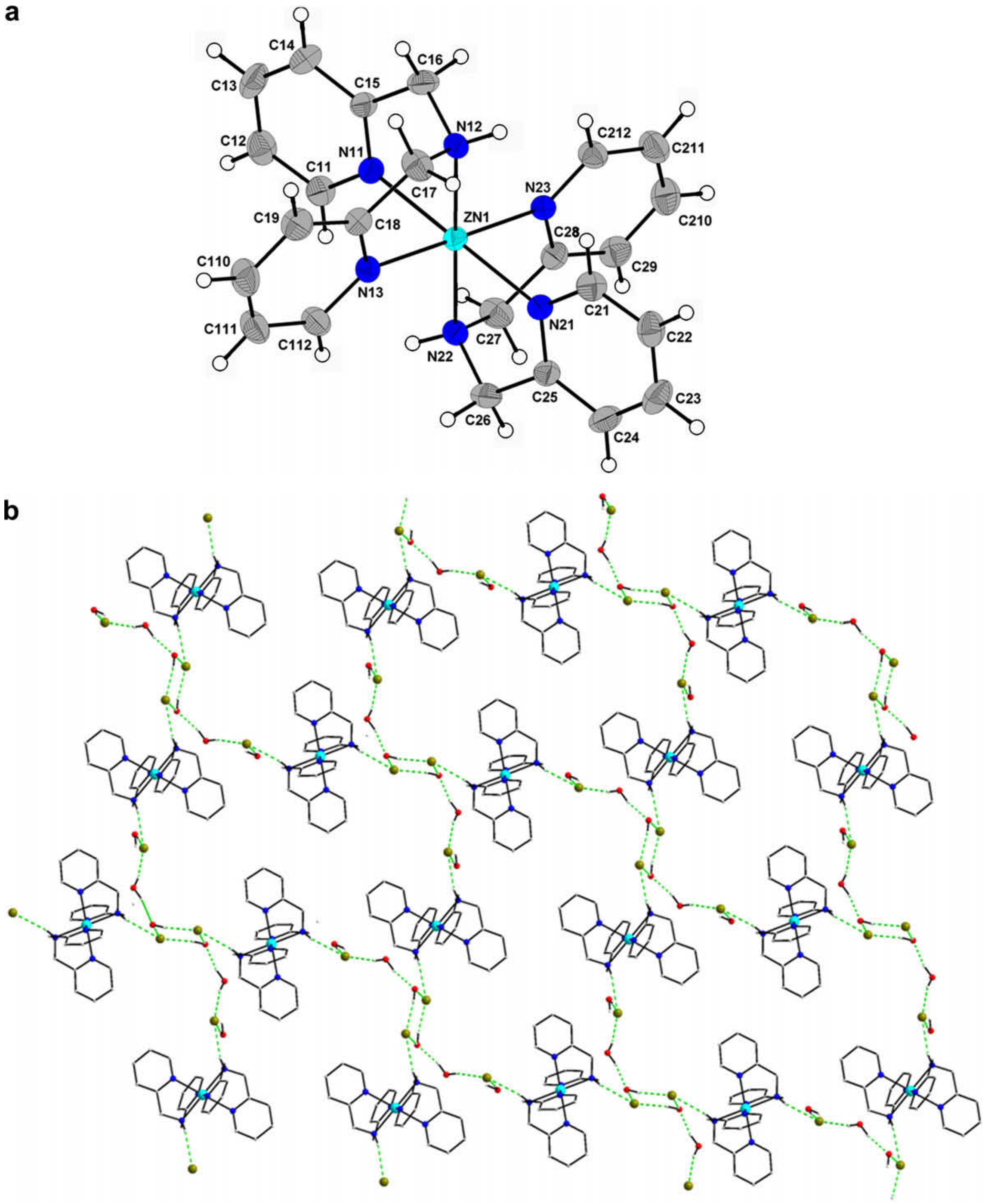


Fig. 2. (a) Structure of the cation of compound **2**. Displacement ellipsoids are shown at the 30% probability level. (b) Hydrogen bond interactions in a two-dimensional polymeric compound. H atoms not involved in intermolecular interactions have been omitted for clarity. Green dotted lines represent N_{amine}–H···Br, O_{water}–H···O_{water} and O_{water}–H···Br hydrogen bonds.(For interpretation of color mentioned in this figure the reader is referred to the web version of the article.)

Table 5
Hydrogen bonds for compound **2** (Å and °)

D–H…A	*d*(D–H)	*d*(H…A)	*d*(D…A)	⟨(DHA)
O(1S)–H(1B)…O(2S)	0.930(2)	1.809(14)	2.717(5)	165(5)
O(3S)–H(3B)…Br(2)#1	0.930(2)	2.442(6)	3.369(4)	175(5)
N(12)–H(12N)…Br(1)#2	0.86(3)	2.56(3)	3.372(3)	158(3)
O(2S)–H(2A)…Br(1)#3	0.930(2)	2.394(9)	3.314(3)	170(4)
O(2S)–H(2B)…Br(1)#4	0.930(2)	2.451(13)	3.363(4)	167(4)
O(1S)–H(1A)…Br(2)#5	0.930(2)	2.445(11)	3.359(3)	167(4)
N(22)–H(22N)…Br(2)#6	0.84(3)	2.57(3)	3.382(3)	164(3)

Symmetry transformations used to generate equivalent atoms: #1 $x, -y + 1/2, z + 1/2$; #2 $-x + 1, -y + 1, -z + 2$; #3 $-x + 1, -y + 2, -z + 1$; #4 $x, y, z - 1$; #5 $x, y + 1, z$; #6 $x + 1, -y + 1/2, z + 1/2$.

3.2. Structure description

The geometry at the zinc atom of all three complexes is pseudo-octahedral, as expected, and three Zn(II) complexes with tridentate bispicam ligand produced *fac* isomers represented (a) above among three potential geometrical isomers ((a) *facial* isomer, (b) *meridional* isomer, and *facial* (c) and (d) isomers which are enantiomers to each other) [7].

The zinc atom in **1** lies on an inversion center giving the C_i isomer as shown in Fig. 1a. The geometry at zinc atom is pseudo-octahedral, and the isomer isolated is the *fac* isomer represented (a) above. The Zn–N$_{amine}$ bond of length 2.153(3) Å is shorter than

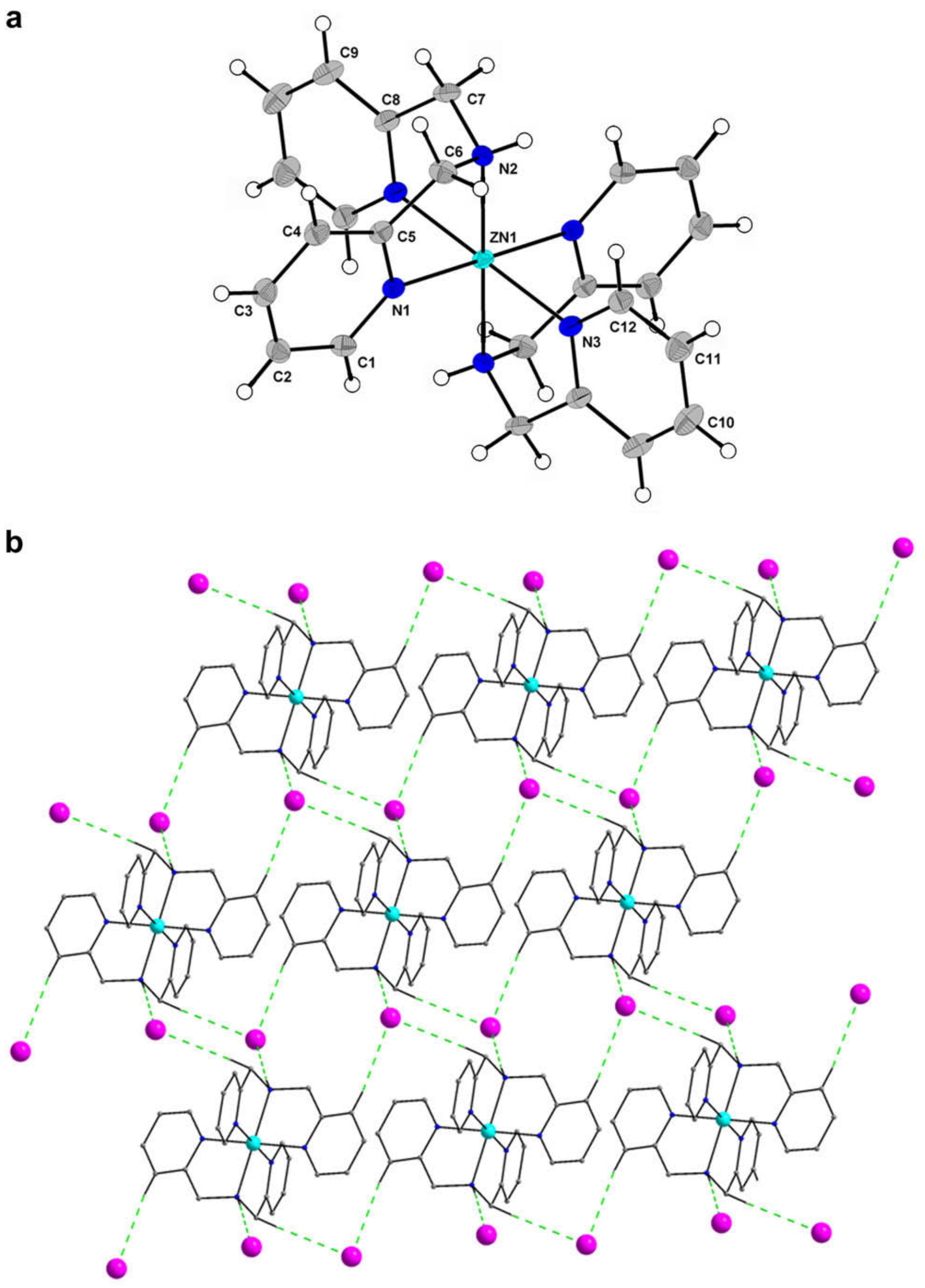


Fig. 3. (a) Structure of the cation of compound **3**. Displacement ellipsoids are shown at the 30% probability level. (b) Hydrogen bond interactions in a two-dimensional polymeric compound. H atoms not involved in intermolecular interactions have been omitted for clarity. Green dotted lines represent N$_{amine}$–H···I and C–H···I hydrogen bonds..(For interpretation of color mentioned in this figure the reader is referred to the web version of the article.)

Table 6
Selected bond lengths [Å] and angles [°] for compound **3**

Zn(1)–N(2)#1	2.159(3)	Zn(1)–N(2)	2.159(3)
Zn(1)–N(1)	2.172(3)	Zn(1)–N(1)#1	2.172(3)
Zn(1)–N(3)#1	2.186(3)	Zn(1)–N(3)	2.186(3)
N(2)#1–Zn(1)–N(2)	180.0	N(2)#1–Zn(1)–N(1)	99.92(11)
N(2)–Zn(1)–N(1)	80.08(11)	N(2)#1–Zn(1)–N(1)#1	80.08(11)
N(2)–Zn(1)–N(1)#1	99.92(11)	N(1)–Zn(1)–N(1)#1	180.0
N(2)#1–Zn(1)–N(3)#1	100.61(12)	N(2)–Zn(1)–N(3)#1	79.39(12)
N(1)–Zn(1)–N(3)#1	86.32(11)	N(1)#1–Zn(1)–N(3)#1	93.68(11)
N(2)#1–Zn(1)–N(3)	79.39(12)	N(2)–Zn(1)–N(3)	100.61(12)
N(1)–Zn(1)–N(3)	93.68(11)	N(1)#1–Zn(1)–N(3)	86.32(11)
N(3)#1–Zn(1)–N(3)	180.0		

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y, -z+2$.

Table 7
Hydrogen bonds for compound **3** (Å and °)

D–H...A	d(D–H)	d(H...A)	d(D...A)	∠(DHA)
C(4)–H(4)...I(1)#2	0.93	3.059(2)	3.967(4)	165.66(1)
C(7)–H(7A)...I(1)	0.97	3.076(1)	3.970(4)	153.95(1)
N(2)–H(2N)...I(1)#3	0.81(4)	2.786(1)	3.585(3)	171.72(1)

Symmetry transformations used to generate equivalent atoms: #1 $-x+1, -y, -z+2$; #2 $x-1, y, z$; #3 $-x+1, -y+1, -z+2$.

two Zn–N$_{pyridyl}$ bonds of 2.166(3) and 2.203(4) Å (Table 2). With chloride anions, O$_{water}$–H···Cl interactions generate flat 4-membered Cl_2O_2 rings, and these 4-membered Cl_2O_2 rings are connected to $[Zn(bispicam)_2]^{2+}$ units through N$_{amine}$–H···Cl interactions to form an one-dimensional polymeric compound as shown in Fig. 1b (Table 3). The 4-membered rings are also connected to other water molecules through O$_{water}$–H···Cl interactions. To the best our knowledge, such an arrangement has not been experimentally observed so far although cyclic $(H_2O)_4$ units have been reported [9].

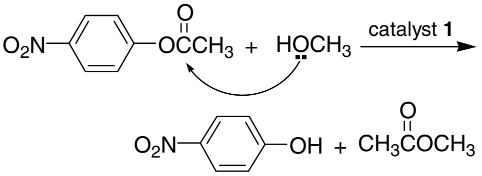
The asymmetric unit of **2** contains a whole molecule, and the structure of **2** is very similar to that of **1** with the *fac* isomer represented (a) above (Fig. 2a). The principle bond distances and angles of **2** are listed in Table 4. The Zn–N distances range from 2.157(3) to 2.184(3) Å. With bromide anions, O$_{water}$–H···Br interactions generate 4-membered Br_2O_2 rings. These Br_2O_2 rings are connected to $[Zn(bispicam)_2]^{2+}$ units through N$_{amine}$–H···Br interactions, and they are also connected to other water molecules through O$_{water}$–H···O$_{water}$ interactions. The connected water molecules are connected to free bromide anions through O$_{water}$–H···Br interactions. The free bromide anions are connected to other $[Zn(bispicam)_2]^{2+}$ units through N$_{amine}$–H···Br interactions. These O$_{water}$–H···Br and N$_{amine}$–H···Br interactions produce 28-membered rings to form a two-dimensional sheet as shown in Fig. 2b (Table 5).

The zinc atom in **3** also lies on an inversion center giving the C_i isomer as shown in Fig. 3a. The structure of **3** is also very similar to that of **1** with the *fac* isomer represented (a) above, and the principle bond distances and angles of **2** are listed in Table 6. With iodide anions, N$_{amine}$–H···I and C–H···I interactions between free iodide anions and $[Zn(bispicam)_2]^{2+}$ units generate 6-membered $Cl_2C_2N_2$ rings to form a two-dimensional sheet as shown in Fig. 3b (Table 7).

To our knowledge, the system containing C/N/O–H···X (X = Cl, Br and I) hydrogen bonding between free (full negative charged) halides and Zn(II) complex cations is unprecedented even though metal-assisted hydrogen bonding (C–H···X–M) is well documented [3,4]. With chloride anions, O$_{water}$–H···Cl interactions generate flat 4-membered Cl_2O_2 rings that are connected to $[Zn(bispicam)_2]^{2+}$ units through N$_{amine}$–H···Cl interactions to form an one-dimensional polymeric compound. With bromide anions, N$_{amine}$–H···Br and O$_{water}$–H···Br interactions generate a two-dimensional sheet. With iodide anions, N$_{amine}$–H···I and C–H···I interactions generate 6-membered $Cl_2C_2N_2$ rings to form a two-dimensional sheet. These results indicate 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 play very important roles for construction of molecular packing and crystal structures.

*3.3. Catalytic transesterification reactions by the compounds **1–3***

We have recently reported that hydrogen-bonded polymers, $Zn(Hdpa)Cl_2$, $Zn(Hdpa)Br_2$ and $Zn(Hdpa)I_2$, formed from the reaction of ZnX_2 ($X = Cl^-$, Br^- and I^-) with a chelating ligand Hdpa have shown, surprisingly, unusual heterogeneous catalytic activities on transesterification reaction of a range of esters with methanol at room temperature under the mild conditions [6]. This result led us to attempt the transesterification reaction using the compounds **1**, **2**, and **3**. Treatment of 4-nitrophenyl acetate and methanol in the presence of the catalysts at 50 °C produced methyl acetate quantitatively under the neutral conditions within 1 day (Eq. (1); see entry 1 of Table 8), respectively, while trace or a small amount of transesterification occurs without each catalyst (the sixth column) [10].



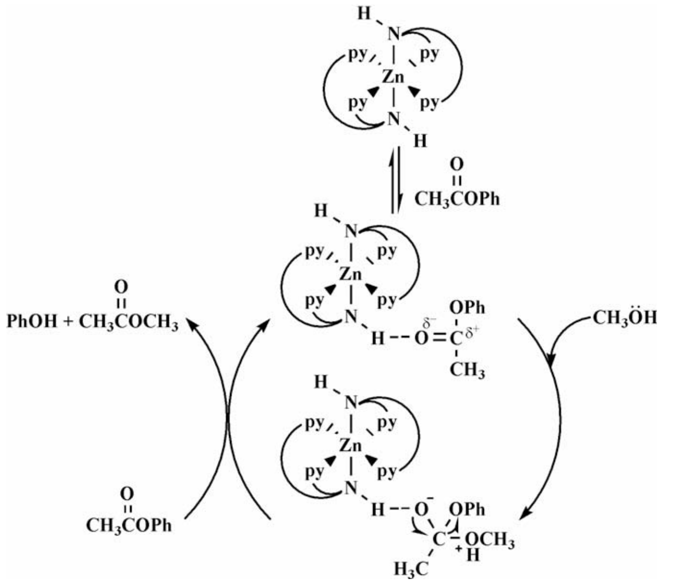
(1)

Based on these results, we have examined the catalytic activity of the hydrogen-bonded polymeric compounds **1**, **2**, and **3** for transesterification of various esters. The results are also given in

Table 8
Transesterification of esters by methanol in the presence of compounds **1**, **2**, and **3** at 50 °C[a]

Entry	Substrate	**1** (time/days)	**2** (time/days)	**3** (time/days)	Control[b] (time/days)
1	4-Nitrophenyl acetate	1	1	1	1 (10%)
2	Phenyl acetate	4	4	2	4 (5%)
3	4-Nitrophenyl benzoate[c]	11	3	6	11 (8%)
4	4-Chlorophenyl benzoate	4	4	2	4 (30%)
5	Phenyl benzoate	13	7	4	13 (25%)
6	4-Methylphenyl benzoate	4	7	3	7 (15%)
7	Vinyl acetate	0.21	0.08	0.08	1 (10%)

[a] All esters were completely converted to the corresponding products, methyl acetate and methyl benzoate. Reaction conditions: esters; 0.05 mmol, catalyst; 1.56×10^{-3} mmol for **1**, 1.44×10^{-3} mmol for **2**, and 1.28×10^{-3} mmol for **3**, solvent; methanol (1 mL). See the experimental section for the detailed reaction conditions.
[b] The transesterification reactions of esters were carried out without the catalysts. Numbers in parentheses indicate the conversion yields of esters to products within a given time.
[c] The solvent was a mixture of CH_3OH/CH_2Cl_2 (1/1) because of low solubility of substrate in CH_3OH.



Scheme 2.

Table 8. Phenyl acetate have displayed slower reactivities than *p*-nitrophenyl acetate by these catalysts with 4, 4 and 2 day reaction time, respectively (entry 2). These catalysts **1**–**3** were also active to benzoates with an electron-donating or -withdrawing group that underwent the transesterification with 2–11 days (entries 3–6). The substrates with the electron-withdrawing substituents have undergone faster transesterification (entries 3 and 4), while those with the electron-donating ones have shown slow reaction (entry 6). Moreover, vinyl acetate, that is widely used as a precursor for ester synthesis [11], was also converted efficiently to the product methyl acetate by the catalysts **1**–**3** within 0.21–0.38 day (entry 7), 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 are able to propose the possible transesterification reaction mechanism based on the structure of the complexes **1**, **2** and **3**. 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, because the hydrogen atom could be acidic by coordinating of nitrogen of N–H to zinc ion (Scheme 2). 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 methanol to produce the product methyl ester as shown in Scheme 2. Detailed mechanistic studies are currently under investigation.

4. Conclusions

$[Zn(bispicam)_2]^{2+}$ as a hydrogen-bond donor and three zinc halides ($ZnCl_2$, $ZnBr_2$ and ZnI_2) as hydrogen-bond acceptors were employed to investigate the role of non-classical C/N–H···X hydrogen bonding for construction of polymeric compounds. 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. This system containing C/N/O–H···X (X = Cl, Br and I) hydrogen bonding between free halides and Zn(II) complex cations is unprecedented even though metal-assisted hydrogen bonding (C–H···X–M) is well documented. We have also reported that Zn-containing hydrogen-bonded polymers **1**, **2** and **3** could carry out the catalytic transesterification of a range of esters with methanol under the mild conditions. Though all these compounds are saturated with two bispicam ligands, interestingly, they have shown the efficient transesterification reactions. To explain this unusual reactivity, it has been proposed that the hydrogen atom of amine N–H moiety in the complexes could do the acid-catalyzed transesterification. Further explorations into the uses of this catalyst family in organic transformations as well as mechanistic investigations are under study.

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