Anion effects on construction of cadmium(II) compounds with a chelating ligand bis(2-pyridylmethyl)amine: Their photoluminescence and catalytic activities

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ABSTRACT

Four new structures of Cd[II] complexes containing bis(2-pyridylmethyl)amine (bispicam) ligands have been determined. Chloride anions bridge two Cd[II] ions to form a dinuclear complex $[(Cd(bispicam)Cl)_2(\mu_2\text{-}Cl_2)]$ (**1**), and bromide and iodide ions produce two halide-coordinated $[Cd(bispicam)X_2]$ complexes (X = Cl for **2** and Br for **3**). Nitrate anions produce both nitrate-coordinated $[Cd(bispicam)_2(NO_3)]^+$ and simple [*mer*-$Cd(bispicam)_2]^{2+}$ with three nitrate counter-anions (**4**). These results indicate that anion effects play very important roles for construction of crystal structures and geometrical isomerism. Moreover, the homogeneous catalyst $[Cd(bispicam)_2](ClO_4)_2$ (**5**) catalyzed efficiently the transesterification of a variety of esters with methanol, while rest of the complexes have displayed very slow conversions. Furthermore, **1–5** showed the intense emissions at room temperature, which could be used as a good candidate for a potential hybrid inorganic–organic photoactive material.

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1. Introduction

Much interest has recently been focused on the self-assembly process for construction of coordination networks [1–6] that has been affected by the hydrogen bonds [7–13], π–π stacking [14], and anions [15–19] as well as ligand design [20] and metal ions [21,22]. Among them, anion effects play very important roles for construction of crystal structures and geometrical isomerism [23–26]. For examples, bis(2-pyridylmethyl)amine (bispicam), a tridentate ligand with the two terminal N-donor coordination sites (pyridyl) and the central N-donor site (amine), can coordinate to metal ions to provide complexes of the general formulation $[M(bispicam)_2]X_2$. For this type of complex system, there are three potential geometric isomers (Scheme 1): facial isomer, meridional isomer, and enantiomers [23,24]. In our previous study, several Zn[II] complexes of the general formulation $[Zn(bispicam)_2]X_2$ (X = Cl^{−} [23], Br^{−} [24], I^{−} [24], NO_3^{−} [25], ClO_4^{−} [23] and OTf[−] [25]) have been obtained, and there were *fac* geometric isomers or enantiomers according to anions. With halides, $[Zn(bispicam)_2]^{2+}$ cations have only *fac* geometric isomer. With coordinating NO_3^{−} anion, a nitrate-coordinated Zn[II] complex of the formulation $[Zn(bispicam)(NO_3)_2]$ was obtained, and when the benzoate was applied with Zn(NO_3)_2, typical $[Zn(bispicam)_2]^{2+}$ cation was obtained and showed *fac* geometric isomer. With non-coordinating ClO_4^{−} and OTf[−] anions, there were *fac* isomers and enantiomers [25].

Another chelating ligand, 2,2′-dipyridylamine (Hdpa), showed to form mononuclear Zn[II] complexes by the reaction with zinc salts [26–30], and then these Zn[II] complexes could 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. In addition, we have shown six new structures of Cd[II] complexes containing Hdpa ligands to study anion effects [31]. With chloride and bromide, Cd[II] ions produce halide-bridged dinuclear units while CdI_2 produces a mononuclear unit without halide-bridging. Cd[II] ions produce mono-Hdpa complex with chelating benzoate, di-Hdpa complex with coordinating NO_3^{−} anion, and tri-Hdpa complexes with non-coordinating ClO_4^{−} and BF_4^{−} anions. Three-dimensional structures of Cd[II]-Hdpa complexes can be produced by hydrogen bonding and π–π interactions. These results also indicate that both inter-molecular hydrogen bonds and π–π interactions as well as anion effects play very important roles in the construction of crystal structures in both Zn[II] and Cd[II] systems [31]. In addition, many of all these complexes catalyzed efficiently the transesterification of a variety of esters with methanol, and Zn complexes showed generally better reactivities than Cd complexes. Moreover, most of Zn and Cd complexes, especially ones with d[10] metal centers, showed the luminescent properties.

To further investigate anion and metal effects on construction of a variety of metal complexes containing chelating bispicam

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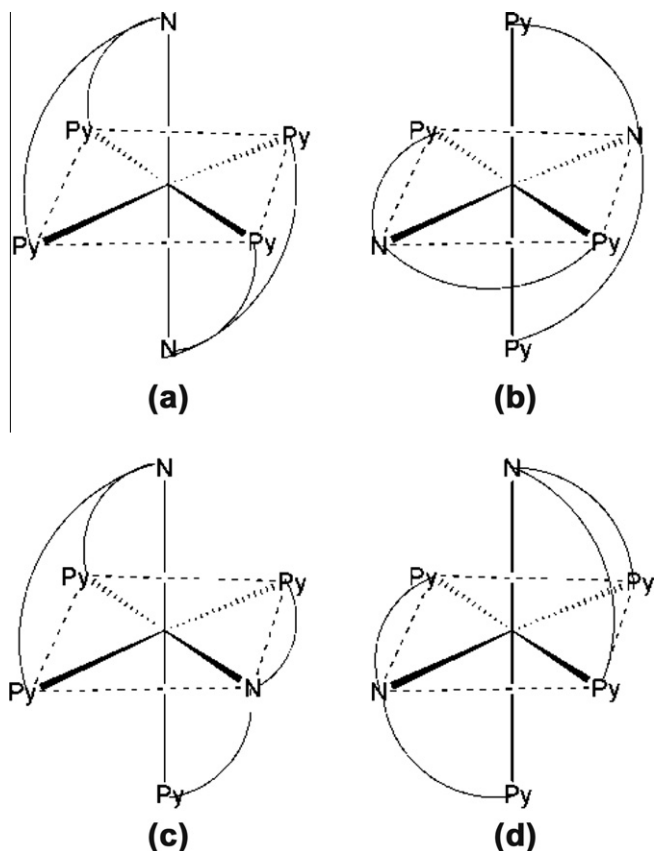
Scheme 1. Three potential geometric isomers of [M(bispicam)$_2$]$^{2+}$.

ligands, and to find efficient catalysts to mediate catalytic transesterification reactions and Cd^{II}-bispicam complexes with photoluminescence properties, therefore, Cd^{II} salts containing several anions (Cl$^-$, Br$^-$, I$^-$, NO$_3^-$, and ClO$_4^-$ [23]) have been applied to this system.

Herein we report the synthesis, crystal structures, catalytic reactivities, and photoluminescence of four new Cd-containing compounds formed by the reaction of the chelating bispicam ligand and four different cadmium salts.

2. Experimental section

2.1. Materials

Methanol, diisopropyl ether, DMF, diethyl ether, methylene chloride, 2,2′-dipicolylamine, 4-nitrophenyl acetate, phenyl acetate, 4-methylphenyl acetate, 4-nitrophenyl benzoate, phenyl benzoate, 4-chlorophenyl benzoate, 4-methylphenyl benzoate, vinyl acetate, methyl acetate, methyl benzoate, cadmium chloride, cadmium bromide, cadmium iodide, cadmium nitrate, and cadmium perchlorate were purchased from Aldrich and were used as received. Nitrophenyl benzoate was obtained from Lancaster.

2.2. Instrumentation

Elemental analysis for carbon, nitrogen, and hydrogen was carried out by using a vario MACRO (Elemental Analysensysteme, Germany) in the Laboratory Center of Seoul National University of Science and Technology, Korea. IR spectra were measured on a BIO RAD FTS 135 spectrometer as KBr pellets. ^{1}H NMR spectra were recorded on a Varian Mercury 400 spectrometer. 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). The emission/excitation spectra were recorded on a Perkin Elmer LS45 fluorescence spectrometer.

2.3. Synthesis of [(Cd(bispicam)Cl)$_2$(μ_2-Cl$_2$)] (1)

35.9 mg (0.125 mmol) of CdCl$_2$ was dissolved in 1 mL solution MeOH/H$_2$O (9:1) and added by 1 mL solution MeOH/H$_2$O (9:1) of 2,2′-dipicolylamine (56.8 mg, 0.25 mmol). Then, on the top of the

Table 1
Crystallographic data for compounds 1–5.

	1	2	3	4	5[a]
Empirical formula	C$_{25}$H$_{30}$Cd$_2$Cl$_4$N$_6$O	C$_{12}$H$_{10}$Br$_2$CdN$_3$	C$_{12}$H$_{10}$CdI$_2$N$_3$	C$_{48}$H$_{52}$Cd$_2$N$_{16}$O$_{12}$	C$_{24}$H$_{26}$CdCl$_2$N$_6$O$_8$
Formula weight	797.15	468.45	562.43	1269.86	709.81
Temperature (K)	170(2)	293(2)	170(2)	170(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Space group	C2/c	P2$_1$/n	P2$_1$/c	P1	C2/c
a (Å)	33.458(2)	8.6592(10)	8.8825(6)	8.5600(8)	20.667(2)
b (Å)	9.2278(6)	27.482(3)	28.850(2)	9.8294(9)	10.9233(11)
c (Å)	23.5759(16)	13.0114(16)	12.9269(10)	15.9871(15)	13.9589(15)
α (°)	90.00	90.00	90.00	86.052(2)	90.00
β (°)	126.0330(10)	108.676(2)	109.2470(10)	78.8910(10)	114.488(2)
γ (°)	90.00	90.00	90.00	84.738(2)	90.00
Volume (Å^3)	5886.2(7)	2933.3(6)	3127.5(4)	1312.6(2)	2867.7(5)
Z	8	8	8	1	4
Density (calc.) (Mg/m^3)	1.799	2.122	2.389	1.606	1.644
Absorption coeff. (mm^{-1})	1.839	6.923	5.332	0.887	1.005
Crystal size (mm)	0.25 × 0.10 × 0.05	0.20 × 0.08 × 0.08	0.15 × 0.05 × 0.03	0.15 × 0.15 × 0.13	0.15 × 0.13 × 0.13
Reflections collected	15 999	16240	17329	7346	7783
Independent reflections	5793 [R(int) = 0.0463]	5720 [R(int) = 0.1138]	6121 [R(int) = 0.0831]	6014 [R(int) = 0.0301]	2804 [R(int) = 0.0330]
Data/restraints/parameters	5793/0/346	5720/0/325	6121/0/325	6014/3/703	2804/0/186
Goodness-of-fit on F^2	0.979	0.816	0.980	1.025	0.952
Final R indices [I > 2σ(I)]	R$_1$ = 0.0260, wR$_2$ = 0.0630	R$_1$ = 0.0463, wR$_2$ = 0.1036	R$_1$ = 0.0390, wR$_2$ = 0.0978	R$_1$ = 0.0373, wR$_2$ = 0.0996	R$_1$ = 0.0365, wR$_2$ = 0.0945
R indices (all data)	R$_1$ = 0.0301, wR$_2$ = 0.0636	R$_1$ = 0.0829, wR$_2$ = 0.1081	R$_1$ = 0.0478, wR$_2$ = 0.1000	R$_1$ = 0.0385, wR$_2$ = 0.1001	R$_1$ = 0.0446, wR$_2$ = 0.0964
Largest difference in peak and hole (e Å^{-3})	0.684 and −0.842	0.962 and −0.924	1.534 and −2.063	1.007 and −1.726	0.529 and −0.824

[a] See Ref. [23].

reaction solution was carefully layered by 6 mL diethyl ether solution. Suitable crystals of compound **1** for X-ray analysis were obtained in a few days. The yield was 16.0 mg (32.1%). ^{1}H NMR (DMSO, 400 MHz): δ 7.45–8.65 (m, 16H, aromatic-H), δ 4.50–4.55 (br, 2H, N–H), and δ 4.00–4.10 (br, 8H, CH$_2$). IR (KBr): ν(cm^{-1}) = 3257(brs, N–H), 1601(s), 1574(w), 1480(m), 1440(s), 1311(w), 1156(w), 1098(w), 1051(w), 1017(w), 985(w), 914(w), 881(w), 762(s), 637(w), 483(w). *Anal.* Calc. for C$_{25}$H$_{30}$Cd$_2$Cl$_4$N$_6$O (797.15), 1: C, 37.67; H, 3.79; N, 10.54. Found: C, 37.35; H, 3.89; N, 10.26%.

2.4. Synthesis of [Cd(bispicam)X$_2$] (X = Br for **2**, I for **3**)

43.9 mg (0.125 mmol) of CdBr$_2$ was dissolved in 1 mL DMF and added by 1 mL DMF solution of 2,2′-dipicolylamine (56.8 mg, 0.25 mmol). Then, on the top of the reaction solution was carefully layered by 6 mL diethyl ether solution. Suitable crystals of compound **2** for X-ray analysis were obtained in a week. The yield was 18.0 mg (30.7%). ^{1}H NMR (DMSO, 400 MHz): δ 7.45–8.15 (m, 8H, aromatic-H), δ 4.55–4.65 (br, 1H, N–H), and δ 4.00 4.15 (br, 4H, CH2). IR (KBr): ν(cm^{-1}) = 3206(brs, N–H), 1602(s), 1573(w), 1483(m), 1442(s), 1287(m), 1155(w), 1097(m), 1049(w), 1017(m), 988(w), 776(s), 640(w). *Anal.* Calc. for C$_{12}$H$_{10}$Br$_2$CdN$_3$ (468.45), 2: C, 30.77; H, 2.15; N, 8.97. Found: C, 30.97; H, 1.87; N, 8.71%.

46.2 mg (0.125 mmol) of CdI$_2$ was dissolved in 1 mL MeOH and added by 1 mL MeOH solution of 2,2′-dipicolylamine (56.8 mg, 0.25 mmol). Then, on the top of the reaction solution was carefully layered by 6 mL methylene chloride solution. Suitable crystals of compound **3** for X-ray analysis were obtained in a few days. The yield was 20.0 mg (28.4%). ^{1}H NMR (DMSO, 400 MHz): δ 7.51–8.67 (m, 8H, aromatic-H), δ 4.60–4.70 (br, 1H, N–H), and δ 4.00–4.20 (br, 4H, CH$_2$). IR (KBr): ν(cm^{-1}) = 3226(brm, N–H), 1601(s), 1573(w), 1480(m), 1440(s), 1284(m), 1153(w), 1097(m), 1048(w), 1015(m), 988(w), 773(s), 728(w), 640(w), 484(w). *Anal.* Calc. for C$_{12}$H$_{10}$CdI$_2$N$_3$ (562.43), 3: C, 25.63; H, 1.79; N, 7.47. Found: C, 25.72; H, 1.52; N, 7.23%.

2.5. Synthesis of [Cd(bispicam)$_2$][Cd(bispicam)$_2$(NO$_3$)](NO$_3$)$_3$ (**4**)

39.3 mg (0.125 mmol) of Cd(NO$_3$)$_2$ was dissolved in 1 mL methanol and added by 1 mL methanol solution of 2,2′-dipicolylamine (56.8 mg, 0.25 mmol). Then, on the top of the reaction solution was carefully layered by 6 mL diisopropyl ether solution. Suitable crystals of compound **4** for X-ray analysis were obtained in a few days. The yield was 20.0 mg (25.2%). ^{1}H NMR (DMSO, 400 MHz): δ 7.35–8.05 (m, 32H, aromatic-H), δ 5.10–5.20 (br, 4H, N–H), and δ 4.10–4.30 (br, 16H, CH$_2$). IR (KBr): ν(cm^{-1}) = 3201(brs, N–H), 2917(w), 1603(m), 1573(w), 1484(w), 1441(m), 1384(s), 1151(w), 1097(w), 1052(w), 1014(w), 913(w), 829(w), 763(m), 637(w), 488(w). *Anal.* Calc. for C$_{48}$H$_{52}$Cd$_2$N$_{16}$O$_{12}$ (1269.86), 4: C, 45.40; H, 4.13; N, 17.65. Found: C, 45.14; H, 4.32; N, 17.30%.

2.6. Catalytic activity of compounds **1**–**5**

Catalytic reaction conditions: Ester (0.05 mmol) was dissolved in methanol (1 mL), and the compounds **1**–**5** (1.0 mg, 1.25 × 10^{-3} mmol for **1**, 1.0 mg, 2.14 × 10 mmol for **2**, 1.0 mg, 1.78 × 10 mmol for **3**, 1.0 mg, 0.79 × 10 mmol for **4**, and 1.0 mg, 1.41 × 10^{-3} mmol for **5**) 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.

Table 2
Selected bond lengths (Å) and angles (°) for compounds **1**–**5**.

1

Cd(1)–N(13)	2.352(2)	Cd(1)–N(12)	2.413(2)
Cd(1)–N(11)	2.417(2)	Cd(1)–Cl(1)	2.5251(7)
Cd(1)–Cl(2)	2.5751(7)	Cd(1)–Cl(3)	2.6722(7)
Cd(2)–N(21)	2.339(2)	Cd(2)–N(23)	2.395(2)
Cd(2)–N(22)	2.414(2)	Cd(2)–Cl(4)	2.4983(7)
Cd(2)–Cl(2)	2.6730(7)	Cd(2)–Cl(3)	2.6758(7)
Cd(1)–Cl(2)–Cd(2)	90.59(2)	Cd(1)–Cl(3)–Cd(2)	88.46(2)
Cl(1)–Cd(1)–Cl(2)	97.17(2)	Cl(1)–Cd(1)–Cl(3)	96.15(2)
Cl(2)–Cd(1)–Cl(3)	89.93(2)	Cl(4)–Cd(2)–Cl(2)	99.55(2)
Cl(4)–Cd(2)–Cl(3)	105.18(2)	Cl(2)–Cd(2)–Cl(3)	87.80(2)

2

Br(11)–Cd(1)	2.5890(10)	Br(12)–Cd(1)	2.5757(11)
Br(21)–Cd(2)	2.6162(10)	Br(22)–Cd(2)	2.5616(10)
Cd(1)–N(11)	2.319(6)	Cd(1)–N(13)	2.328(6)
Cd(1)–N(12)	2.397(10)		
		Cd(2)–N(23)	2.332(6)
Cd(2)–N(21)	2.339(6)	Cd(2)–N(22)	2.397(13)
Br(12)–Cd(1)–Br(11)	112.99(4)	Br(22)–Cd(2)–Br(21)	113.60(4)

3

		Cd(1)–N(11)	2.339(5)
Cd(1)–N(13)	2.348(5)	Cd(1)–N(12)	2.423(12)
Cd(1)–I(11)	2.7427(6)	Cd(1)–I(12)	2.8111(7)
Cd(2)–N(23)	2.340(5)	Cd(2)–N(21)	2.351(5)
Cd(2)–N(22)	2.360(12)		
Cd(2)–I(22)	2.7660(7)	Cd(2)–I(21)	2.7774(6)
I(11)–Cd(1)–I(12)	114.35(2)	I(22)–Cd(2)–I(21)	110.18(2)

4

Cd(1)–N(23)	2.342(7)	Cd(1)–N(11)	2.347(5)
Cd(1)–N(21)	2.356(6)	Cd(1)–N(12)	2.360(7)
Cd(1)–N(22)	2.376(6)	Cd(1)–N(13)	2.379(6)
Cd(2)–N(33)	2.330(7)	Cd(2)–N(31)	2.358(6)
Cd(2)–N(42)	2.370(6)	Cd(2)–N(32)	2.402(5)
Cd(2)–N(43)	2.409(6)	Cd(2)–O(11)	2.452(5)
Cd(2)–N(41)	2.591(5)		
N(23)–Cd(1)–N(11)	99.0(2)	N(23)–Cd(1)–N(21)	142.1(2)
N(11)–Cd(1)–N(21)	89.52(19)	N(23)–Cd(1)–N(12)	112.5(2)
N(11)–Cd(1)–N(12)	70.5(2)	N(21)–Cd(1)–N(12)	105.2(2)
N(23)–Cd(1)–N(22)	72.0(2)	N(11)–Cd(1)–N(22)	120.4(2)
N(21)–Cd(1)–N(22)	71.8(2)	N(12)–Cd(1)–N(22)	168.2(2)
N(23)–Cd(1)–N(13)	90.7(2)	N(11)–Cd(1)–N(13)	140.5(2)
N(21)–Cd(1)–N(13)	105.9(2)	N(12)–Cd(1)–N(13)	70.5(2)
N(22)–Cd(1)–N(13)	99.0(2)	N(33)–Cd(2)–N(31)	118.7(3)
N(33)–Cd(2)–N(42)	92.7(2)	N(31)–Cd(2)–N(42)	139.4(2)
N(33)–Cd(2)–N(32)	71.2(2)	N(31)–Cd(2)–N(32)	71.1(2)
N(42)–Cd(2)–N(32)	148.31(19)	N(33)–Cd(2)–N(43)	158.5(2)
N(31)–Cd(2)–N(43)	81.7(2)	N(42)–Cd(2)–N(43)	72.90(19)
N(32)–Cd(2)–N(43)	113.00(19)	N(33)–Cd(2)–O(11)	90.3(2)
N(31)–Cd(2)–O(11)	81.4(2)	N(42)–Cd(2)–O(11)	72.82(19)
N(32)–Cd(2)–O(11)	132.22(19)	N(43)–Cd(2)–O(11)	100.2(2)
N(33)–Cd(2)–N(41)	87.6(2)	N(31)–Cd(2)–N(41)	131.53(19)
N(42)–Cd(2)–N(41)	69.83(19)	N(32)–Cd(2)–N(41)	82.08(18)
N(43)–Cd(2)–N(41)	72.60(19)		

5

Cd(1)–N(3)#1	2.338(3)	Cd(1)–N(3)	2.338(3)
Cd(1)–N(2)#1	2.340(3)	Cd(1)–N(2)	2.340(3)
Cd(1)–N(1)#1	2.375(3)	Cd(1)–N(1)	2.375(3)
N(3)#1–Cd(1)–N(3)	88.87(15)	N(3)#1–Cd(1)–N(2)#1	73.91(11)
N(3)–Cd(1)–N(2)#1	147.75(11)	N(3)#1–Cd(1)–N(2)	147.75(11)
N(3)–Cd(1)–N(2)	73.91(11)	N(2)#1–Cd(1)–N(2)	133.08(16)
N(3)#1–Cd(1)–N(1)#1	111.00(11)	N(3)–Cd(1)–N(1)#1	90.31(11)
N(2)#1–Cd(1)–N(1)#1	71.63(10)	N(2)–Cd(1)–N(1)#1	96.45(10)
N(3)#1–Cd(1)–N(1)	90.31(11)	N(3)–Cd(1)–N(1)	111.00(11)
N(2)#1–Cd(1)–N(1)	96.45(10)	N(2)–Cd(1)–N(1)	71.63(10)
N(1)#1–Cd(1)–N(1)	150.48(15)		

Symmetry transformations used to generate equivalent atoms: #1 −x + 1, y, −z + 3/2.

2.7. Crystallography

The diffraction data for all five compounds were collected on a Bruker SMART AXS diffractometer equipped with a monochromator in the Mo Kα (λ = 0.71073 Å) incident beam. The crystal was
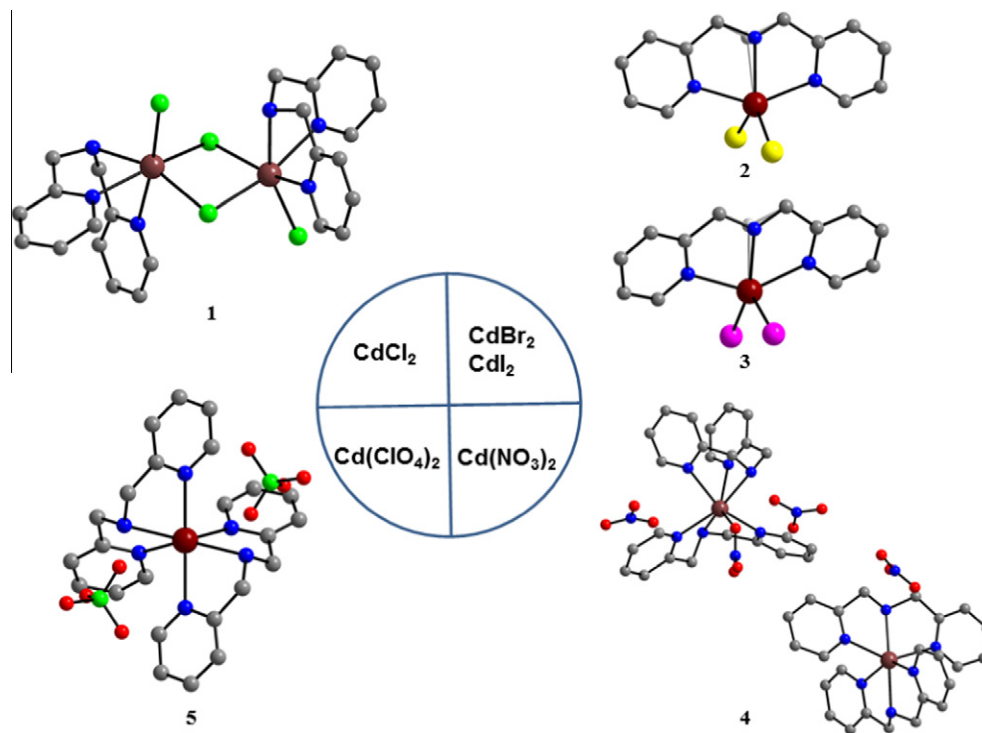
Scheme 2. Structures of Cd^{II} compounds containing bispicam ligands.

mounted on a glass fiber. The CCD data were integrated and scaled using the Bruker-SAINT software package, and the structure was solved and refined using SHEXTL V6.12 [32]. Hydrogen atoms were located in the calculated positions. All hydrogen atoms except hydrogen atoms of water molecules were located in the calculated positions. The crystallographic data for compounds **1–5** are listed in Table 1.

3. Results and discussion

In order to understand the anion effects on the construction of crystal structures with the chelating bispicam ligand, we synthesized four new compounds **1–4**. The previously reported compound **5** has been synthesized again to study anion effects for the Cd^{II}-bispicam system [23]. All five structures including the previously reported **5** have been determined by X-ray crystallography. Table 2 lists the selected bond distances and angles for **1–4**. The structures of all five Cd^{II} compounds containing bispicam ligands are shown in Scheme 2.

3.1. Crystal structure of [(Cd(bispicam)Cl)$_2$(μ_2-Cl$_2$)] **1**

Chlorides act as both a simple coordinating ligand and a bridging ligand to form chloride-bridged dinuclear compound **1** (Fig. 1(a)). There is a methanol solvent molecule per a dinuclear molecule. The geometry around the Cd^{II} ion is distorted octahedral constructed by three N atoms of the chelating bispicam ligand, a simple coordinating chloride, and two bridging chlorides. The Cd–N bond distances range from 2.339(2) to 2.417(2) Å which are a little longer than those of the Cd^{II}-Hdpa system (2.316(4) and 2.333(4) Å) [31]. The Cd–Cl distances are 2.4983(7) and 2.5251(7) Å, which are shorter than the Cd–Cl$_{bridging}$ distances (2.5751(7)–2.6758(7) Å) (Table 2). The C–H⋯Cl intra-molecular hydrogen bonding interactions and the O–H⋯Cl inter-molecular hydrogen bonding interactions produce a polymeric structure

(Fig. 1(b)) and Table 3). In the dinuclear unit in **1**, the Cd–Cl–Cd angles are 88.46(2)° and 90.59(2)°, and the Cd⋯Cd distance is 3.731(1) Å.

3.2. Crystal structures of Cd(bispicam)X$_2$ (X = Br for **2**, I for **3**)

Not like chlorides with bridging ability, bromides and iodides act as simple coordinating ligands in this system. A bispicam ligand and two bromides or iodides coordinate to a Cd^{II} ion to form a distorted trigonal bipyramidal environment, and the amine nitrogen atom is disordered as shown in Fig. 2(a) for **2** and Fig. 3(a) for **3**. The Cd–N bond distances range from 2.296(13) to 2.427(18) Å which are longer than those of the Cd^{II}-Hdpa system (2.259(6)–2.307(7) Å) [31]. The Cd–Br distances range from 2.5616(10) to 2.6162(10) Å, and the Cd–I distances range from 2.7427(6) to 2.8111(7) Å (Table 2). The Br–Cd–Br angles are 112.99(4)° and 113.60(4)°, and the I–Cd–I angles are 110.18(2)° and 114.35(2)°. There are C–H⋯X (X = Br or I) hydrogen bonding interactions in both compounds **2** and **3** (Table 3). The packing diagrams of both compounds are shown in Figs. 2(b) and 3(b), respectively.

3.3. Crystal structures of [Cd(bispicam)$_2$][Cd(bispicam)$_2$(NO$_3$)](NO$_3$)$_3$ (**4**)

An asymmetric unit contains two independent Cd^{II} complex cations: one is Cd^{II} coordinated by two bispicam ligands and the other is Cd^{II} coordinated by two bispicam ligands and a nitrate (Fig. 4(a)). There are three nitrate counter-anions to balance charge. The nitrate coordinated Cd^{II} complex has seven-coordination geometry, and the other Cd^{II} complex has distorted octahedral geometry. This octahedral Cd complex shows *mer* geometry that is the only example for bispicam-containing Cd compounds. The inter-molecular hydrogen bonding interactions provide a polymeric compound (Fig. 4(b) and Table 3). The Cd–N bond distances range from 2.330(7) to 2.591(5) Å which are longer than those of the
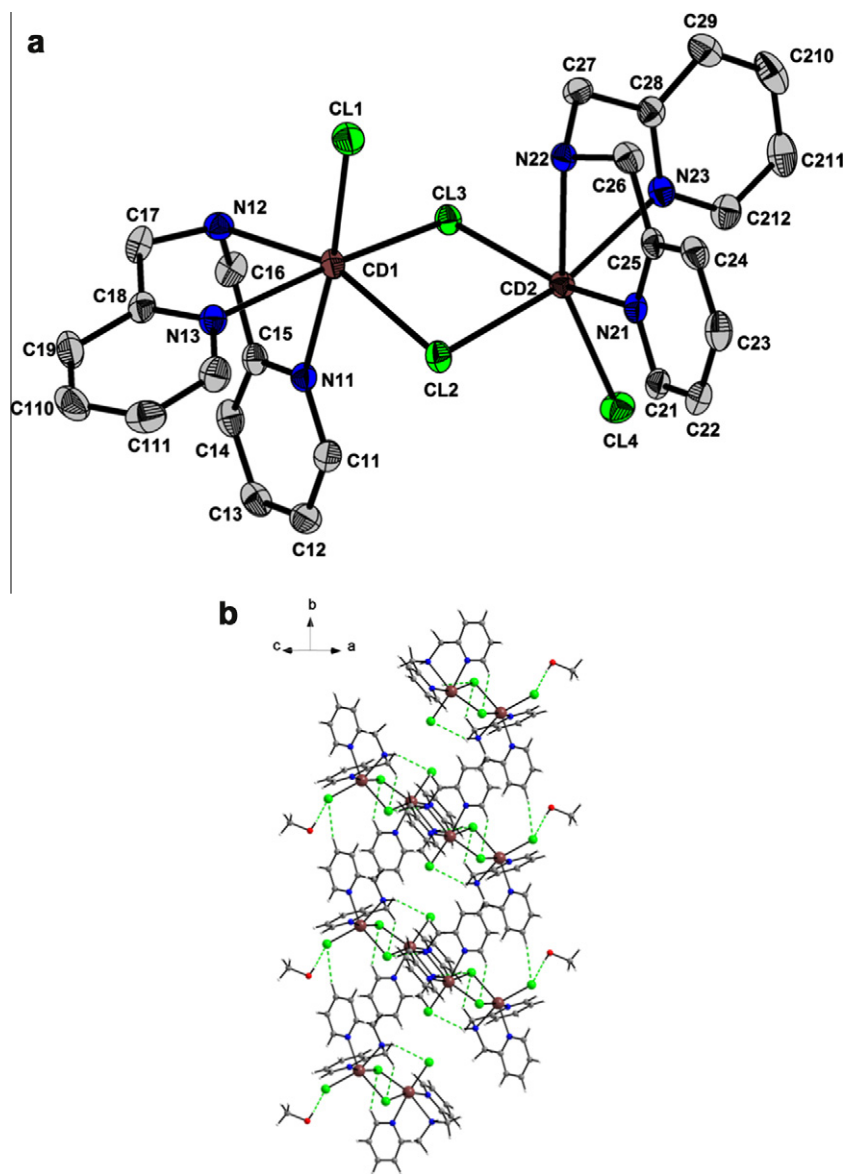
Fig. 1. (a) Structure of **1**. Displacement ellipsoids are shown at the 50% probability level. All hydrogen atoms and methanol solvent molecules were omitted for clarity. (b) Polymeric structure derived by hydrogen bond interactions (green dotted lines). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Cd[II]-Hdpa system (2.315(3) and 2.320(3) Å), and Cd–O$_{nitrate}$ distance is 2.452(5) Å similar to that of the Cd[II]-Hdpa system (2.497(3) Å) (Table 2) [31].

When the chelating bispicam ligands react with various Zn[II] salts (Cl^{−} [23], Br^{−} [24], I^{−} [24], NO$_3^−$ [25], ClO$_4^−$ [23] and OTf[−] [25]), complexes of the general formulation [Zn(bispicam)$_2$]X$_2$ have been obtained, and there were *fac* geometric isomers or enantiomers according to anions. In contrast to Zn[II] system, with Cd[II] salts, various structures (chloride bridged dinuclear, distorted square pyramidal, distorted octahedral and seven-coordinated mononuclear complexes) were observed according to the change of the anions (Scheme 2).

Hdpa has also been used as a chelating ligand to form various Cd[II] complexes [31], and then those Cd[II] complexes can be compared to corresponding Cd[II] complexes containing bispicam ligands. For both chelating Hdpa and bispicam ligands, various anions (halides, nitrate, and perchlorate) have been adopted. For each anion, different structures have been obtained in both

systems as shown in Scheme 3. Halide anions can be used as bridging ligands in both Cd[II]-Hdpa and Cd[II]-bispicam systems. For Cd[II]-Hdpa system, depending on the size of the halide ions, the coordination on Cd[II] ion changes from octahedral in chloride to trigonal bipyramidal in bromide and tetrahedral in iodide. For Cd[II]-bispicam system, only chlorides can show bridging capability, and bigger bromides and iodides simply coordinate to Cd[II] ions to form mononuclear Cd[II] complexes as shown in Scheme 3. In both systems, the bridging capability decreases from chloride down to iodide. Nitrate anions were used as simple O-donor coordinating ligands for Cd[II]-Hdpa system. In Cd[II]-bispicam system, two independent Cd[II]-bispicam complexes were observed: one is nitrate-coordinated Cd(bispicam)$_2$ complex with a free nitrate, and the other is simple [Cd[II](bispicam)$_2$][+] cation complex with two free nitrates. Cd[II] ion is big enough to produce a seven-coordinated complex as well as six-coordinated (octahedral) complex. For non-coordinating ClO$_4^−$ anions, both Hdpa and bispicam ligands produce the cation complexes containing three chelating Hdpa
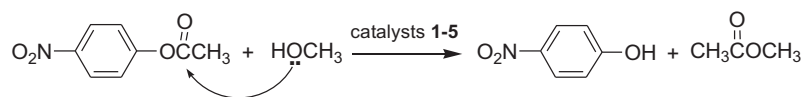
ligands and two chelating bispicam ligands, respectively, with octahedral environments. The perchlorate anions occupy empty positions between cation complexes for charge balances.

3.4. Photoluminescence property

Luminescent compounds are of great current interest because of their various applications in chemical sensors, photochemistry, and electroluminescent display [33]. In addition, coordination polymers containing cadmium and zinc exhibit photoluminescent properties [33,34]. Therefore, the luminescent properties of compounds **1–5** have been investigated. The photoluminescent spectra of compounds **1–5** have been measured in the solid state at room temperature and that of bispicam ligand was measured in the liquid state. Emissions of compounds **1–5** were observed at 421 nm (λ_{ex} = 354 nm) for **1**, 421 nm (λ_{ex} = 357 nm) for **2**, 420 nm (λ_{ex} = 357 nm) for **3**, 397 nm (λ_{ex} = 355 nm) for **4**, and 423 nm (λ_{ex} = 357 nm) for **5**, respectively (Fig. 5), while ligand 2,2′-dicolylamine showed an emission at 424 nm (λ_{ex} = 350 nm). The emissions for the complexes (Fig. 5) except for **4** can be tentatively assigned to the intraligand transition of 2,2′-dipicolylamine ligand, since the similar emission was observed for the ligand. The emission band of complex **4** are blue-shifted compared to the corresponding ligand, which indicates that the emission peak of **4** may be due to the metal-to-ligand charge transfer (MLCT) and/or ligand-to-metal charge transfer (LMCT). In addition, it is noteworthy that **1–5** showed the intense emissions at room temperature, suggesting that they may be a good candidate for a potential hybrid inorganic–organic photoactive material [35].

3.5. Catalytic transesterification reactions by the compounds 1–5

We have previously reported that Zn(Hdpa)X$_2$ (X = Cl$^-$, Br$^-$, I$^-$, $^-$O$_2$CC$_6$H$_5$, NO$_3$$^-$, and SO$_4$$^{2-}$) and Zn(bispicam)$_2Y_2$ (Y = Cl$^-$, Br$^-$, I$^-$, NO$_3$$^-$, ClO$_4$$^-$, and OTf$^-$) complexes could carry out the catalytic transesterification of a range of esters with methanol at room temperature under the mild conditions [24,25,29,30]. Moreover, we have recently shown that [Cd(Hdpa)$_{1-3}$]Z^2 (Z = Cl$^-$, Br$^-$, I$^-$, $^-$O$_2$CC$_6$H$_5$, NO$_3$$^-$, ClO$_4$$^-$, and BF$_4$$^-$) could also catalyzed the transesterification reactions of a series of esters in spite of being well known as an inert metal [31]. In order to compare the reactivity of the complexes containing Zn ion and Cd ion, therefore, we have examined the transesterification reaction with the compounds **1–5**. Thus, the compounds **1–5** were treated with phenyl acetate and methanol at 50 °C under the neutral conditions (Eq. (1)). This reaction produced quantitatively the corresponding product methyl acetate.[1]

Table 3
Hydrogen bonds for compounds **1–5** (Å and °).

D–H···A	d(D–H)	d(H···A)	d(D···A)	<(DHA)
1				
C(23)–H(23)···Cl(4)#1	0.95	2.79	3.557(3)	137.8
N(12)–H(12A)···Cl(3)#2	0.93	2.57	3.453(2)	159.7
O(1S)–H(1S)···Cl(4)	0.84	2.33	3.164(2)	174.4
C(11)–H(11)···Cl(2)	0.95	2.85	3.504(3)	126.9
C(27)–H(27B)···Cl(3)	0.99	2.87	3.510(3)	123.4
N(22)–H(22A)···Cl(1)	0.93	2.67	3.524(2)	153.4
2				
C(210)–H(210)···Br(12)#1	0.93	2.81	3.681(10)	156.6
3				
C(110)–H(110)···I(22)#1	0.95	3.03	3.886(8)	151.1
4				
C(210)–H(210)···O(13)#1	0.95	2.48	3.415(10)	167.1
C(110)–H(110)···O(33)#2	0.95	2.51	3.371(10)	150.4
C(49)–H(49)···O(12)#3	0.95	2.58	3.147(10)	118.7
C(27)–H(27B)···O(41)	0.99	2.38	3.341(10)	162.3
C(412)–H(412)···O(23)	0.95	2.48	3.360(11)	154.6
C(312)–H(312)···O(32)#4	0.95	2.43	3.175(10)	134.9
C(311)–H(311)···O(43)	0.95	2.45	3.160(11)	131.1
C(212)–H(212)···O(33)#5	0.95	2.43	3.372(10)	174.0
C(212)–H(212)···O(31)#5	0.95	2.50	3.189(10)	129.2
C(42)–H(42)···O(13)#6	0.95	2.53	3.259(9)	133.8
C(37)–H(37B)···O(13)#1	0.99	2.57	3.552(9)	170.0
C(31)–H(31)···O(22)#4	0.95	2.55	3.484(13)	166.9
C(29)–H(29)···O(32)	0.95	2.40	3.352(12)	174.9
C(23)–H(23)···O(13)#7	0.95	2.47	3.408(9)	169.0
C(13)–H(13)···O(21)#8	0.95	2.45	3.379(10)	165.4
N(42)–H(42A)···O(32)#4	0.93	2.36	3.191(10)	148.2
N(42)–H(42A)···O(31)#4	0.93	2.38	3.097(8)	133.4
N(32)–H(32A)···O(23)	0.93	2.46	3.295(9)	149.0
N(32)–H(32A)···O(22)	0.93	2.24	3.030(9)	142.9
N(22)–H(22A)···O(43)#1	0.93	2.22	3.053(9)	149.3
N(22)–H(22A)···O(42)#1	0.93	2.24	3.035(8)	143.0
N(12)–H(12A)···O(33)#5	0.93	2.02	2.934(8)	168.2
5				
C(6)–H(6B)···O(3)#2	0.97	2.51	3.335(5)	143.1
C(6)–H(6A)···O(2)	0.97	2.55	3.255(6)	129.6
C(3)–H(3)···O(2)#3	0.93	2.53	3.367(6)	150.5
N(2)–H(2A)···O(1)	0.91	2.13	3.033(4)	171.1

Symmetry transformations used to generate equivalent atoms of **1**: #1 $x, y + 1, z$; #2 $-x + 1/2, -y + 1/2, -z + 1$.
Symmetry transformations used to generate equivalent atoms of **2**: #1 $x - 3/2, -y + 3/2, z + 1/2$.
Symmetry transformations used to generate equivalent atoms of **3**: #1 $-x + 2, -y + 2, -z + 1$.
Symmetry transformations used to generate equivalent atoms of **4**: #1 $x - 1, y, z$; #2 $x - 1, y - 1, z$; #3 $x, y + 1, z$; #4 $x + 1, y, z$; #5 $x, y - 1, z$; #6 $x - 1, y + 1, z$; #7 $x - 1, y, z - 1$; #8 $x + 1, y - 1, z - 1$.
Symmetry transformations used to generate equivalent atoms of **5**: #1 $-x + 1, y, -z + 3/2$; #2 $x, -y + 2, z + 1/2$; #3 $-x + 1, -y + 2, -z + 2$.

O$_2$N—⟨⟩—O–C(=O)CH$_3$ + HOCH$_3$ →(catalysts **1-5**)→ O$_2$N—⟨⟩—OH + CH$_3$C(=O)OCH$_3$ (1)

Compound **5** has shown a moderate catalytic reactivity (6 days; see Table 4), while rest of the complexes have displayed very slow conversions (17–30 days; data not shown). The catalytic reactivity of **5** is three times slower than that of the corresponding Zn complexes [23], confirming the fact that the second period transition metals

are less labile for the substitution reaction. Moreover, **5** showed six times slower activity than the corresponding Cd complexes containing Hdpa ligand [31]. This difference might be explained by the electron density of metal center. Cadmium ion center of **5** would be more electron-rich than that of [Cd(Hdpa)$_3$](ClO$_4$)$_2$ complex, because the electron-rich central-amine of the ligand bispicam in **5** coordinates to the Cd center, while the central amine of Hdpa in [Cd(Hdpa)$_3$](ClO$_4$)$_2$ is not involved in the coordination sphere. Therefore, **5** having more electron-rich Cd center might show slower catalytic reactivity
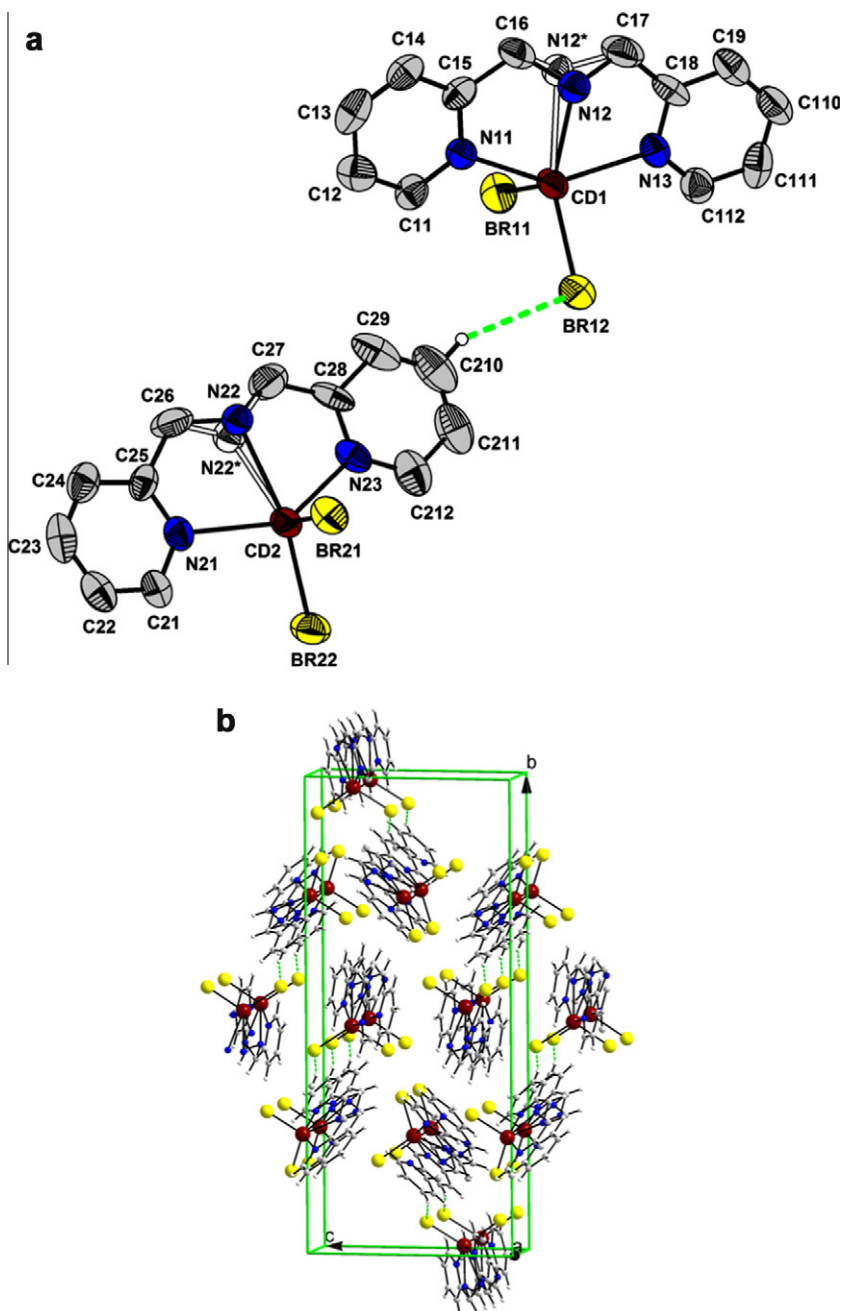
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[1] A control reaction carried out in absence of the complexes showed trace amounts of the conversion of the ester to the product in the same time period.

Fig. 2. (a) Structure of **2**. Displacement ellipsoids are shown at the 50% probability level. The disordered amine N atom is shown. The C–H···Br hydrogen bond interaction (green dotted lines) is shown. All hydrogen atoms except a hydrogen bonding atom were omitted for clarity. (b) Packing diagram of **2**. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

than the corresponding [Cd(Hdpa)$_3$](ClO$_4$)$_2$ having more electron-deficient Cd center.

As **5** showed the moderate catalytic reactivity for the transesterification reaction of phenyl acetate with methanol, we have investigated the transesterification of various p-substituted phenyl acetates and benzoates with it (Table 4). The substrates with the electron-withdrawing substituents have undergone faster transesterification (entries 1 and 4), while those with the electron-donating ones have shown slow reaction (entries 3 and 7). It is worthwhile to note that in the presence of **5**, p-substituted phenyl benzoates have undergone 2–10 times faster transesterification reactions than p-substituted phenyl acetates, unlike the transesterification reaction results previously shown in zinc and cadmium

complexes with Hdpa ligand [29–31]. These results suggest that **5** could be used to carry out efficient transesterification reaction of phenyl benzoates, which are known as difficult substrates. Vinyl acetate, which is widely used as a precursor for ester synthesis [24,25,29–31], was also converted efficiently to the product methyl acetate within 0.4 days by the catalyst (entry 8).

Based on the structure of **4** containing both seven-coordinated Cd^{II} complex and octahedral Cd^{II} complex, we are able to propose a possible reaction mechanism for **5**-catalyzed transesterification. Though **5** has the saturated structure without a labile ligand, the seven-coordination on Cd^{II} suggests that the substrate ester might coordinate to cadmium ion of the complex acting as Lewis acid. Therefore, the Cd center interacts with the oxygen atom of carbonyl
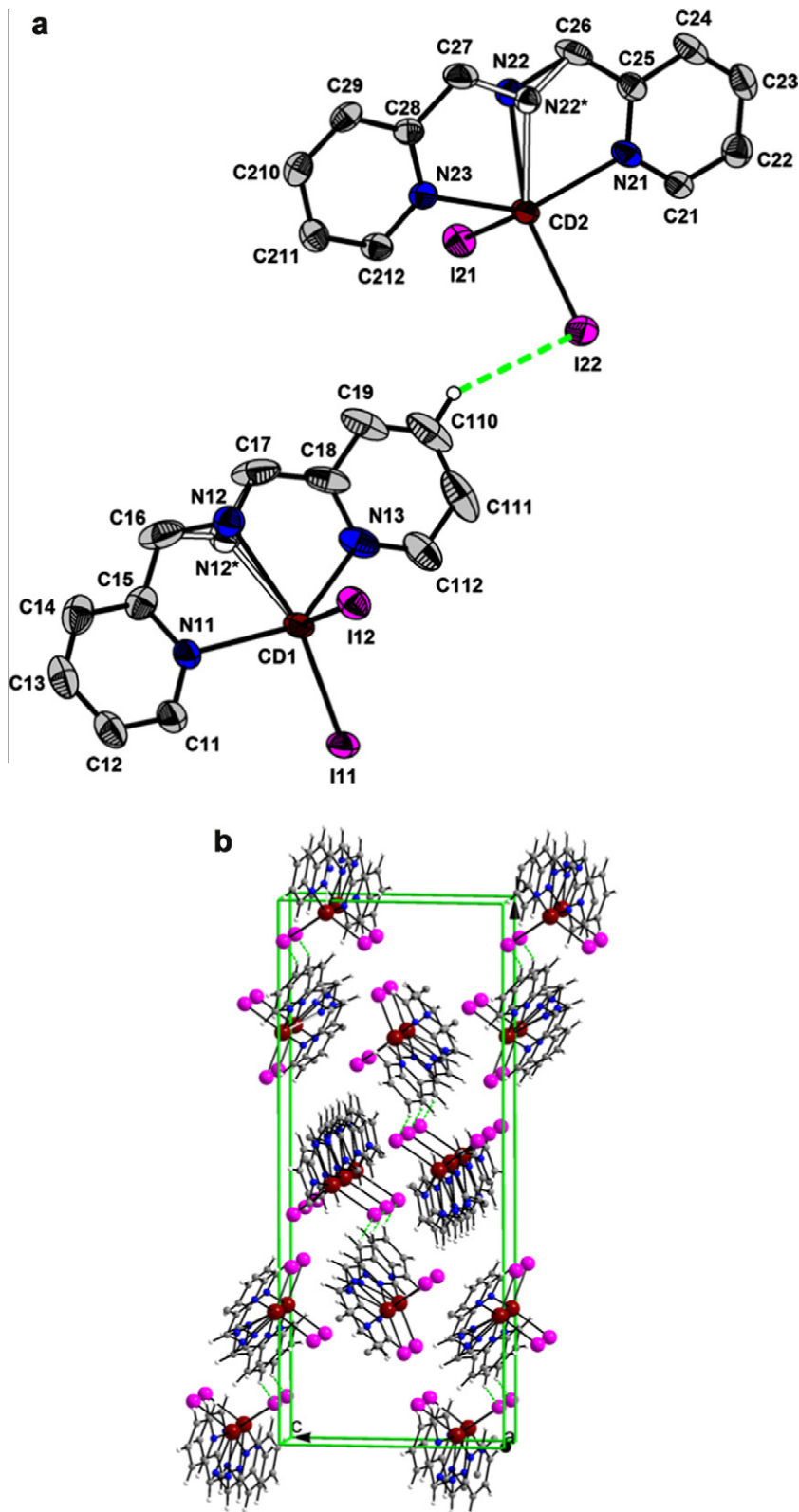
Fig. 3. (a) Structure of **3**. Displacement ellipsoids are shown at the 50% probability level. The disordered amine N atom is shown. The C–H···I hydrogen bond interaction (green dotted lines) is shown. All hydrogen atoms except a hydrogen bonding atom were omitted for clarity. (b) Packing diagram of **3**. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

of ester, making the carbonyl more electrophilic. Then, the nucleophile methanol could attack the resulting activated carbonyl group to produce the product methyl ester as shown in Scheme 4.

Moreover, as shown in Table 4, the fact that the substrates with the electron-withdrawing substituents have undergone faster transesterification, suggests that the second step in Scheme 4, the
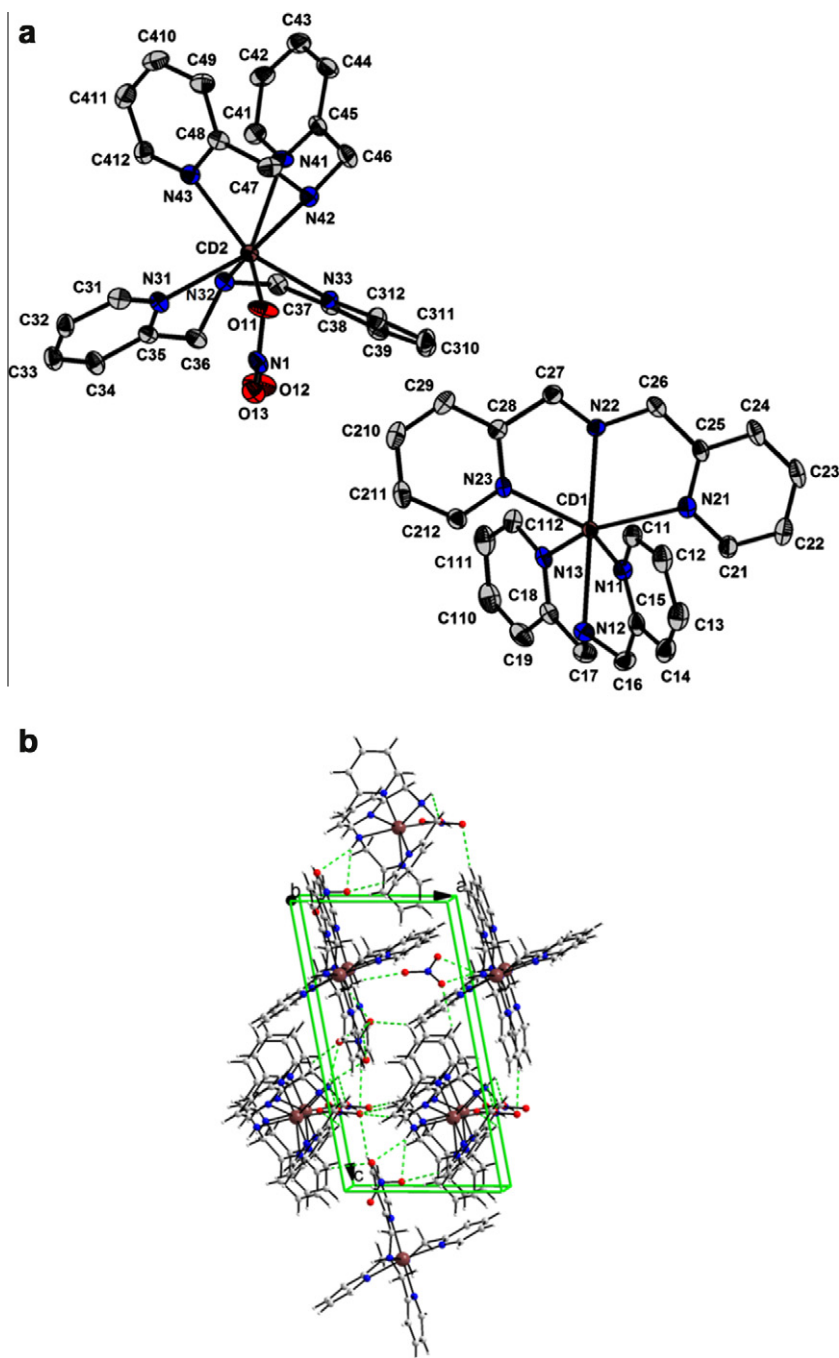
Fig. 4. (a) Structure of **4**. Displacement ellipsoids are shown at the 30% probability level. All hydrogen atoms and nitrate counter-anions were omitted for clarity. (b) The hydrogen bond interactions in a unit cell (green dotted lines). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

attack of the nucleophile methanol into the resulting activated carbonyl group, is the rate-determining step. If the first step is the rate-determining step, the presence of the electron-withdrawing groups on the phenyl ring of substrate would destabilize the first reaction intermediate, resulting in slower transesterification reactions.

There is another possible mechanism that cannot be ruled out. The hydrogen atom of amine N–H moiety in the complex **5** acts as the general-acid catalyst as previously proposed [24,25], because the hydrogen atom could be acidic by coordinating of nitrogen of N–H to cadmium ion (Scheme 5). As **5** has the saturated structure without a labile ligand, we presume that the substrate ester does not coordinate to zinc ion of the complex acting as Lewis acid, unlike

the former proposed mechanism. Therefore, we propose that this acidic hydrogen interacts with the oxygen atom of carbonyl of ester, making the carbonyl more electrophilic. As proposed in the former mechanism (Scheme 4), then, the nucleophile methanol could attack the resulting activated carbonyl group to produce the product methyl ester. More detailed mechanistic studies to figure out the reaction mechanism are in progress in our laboratory.

4. Conclusions

Four new structures of Cd[II] complexes containing bispicam ligands have been determined. For chloride, chloride bridging dinuclear complex [(Cd(bispicam)Cl)$_2$(μ_2-Cl$_2$)] with octahedral
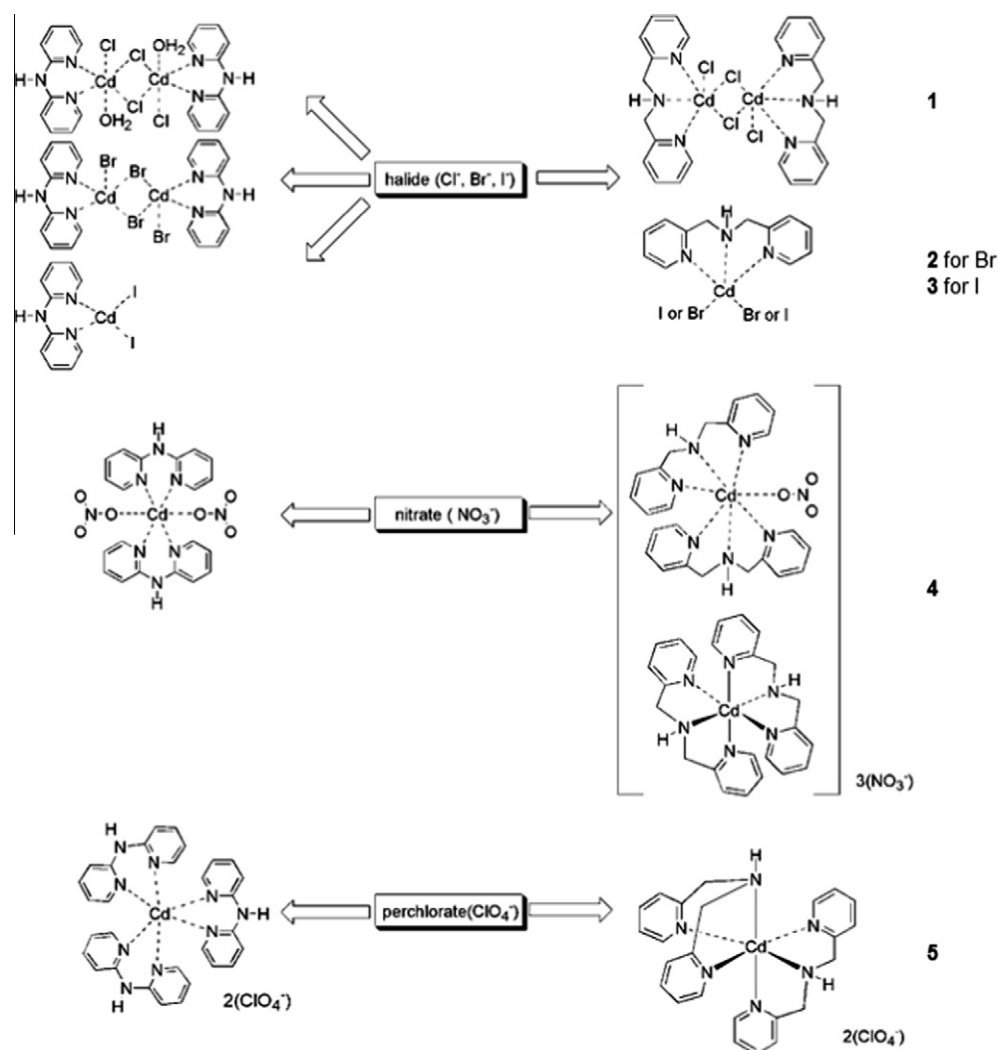
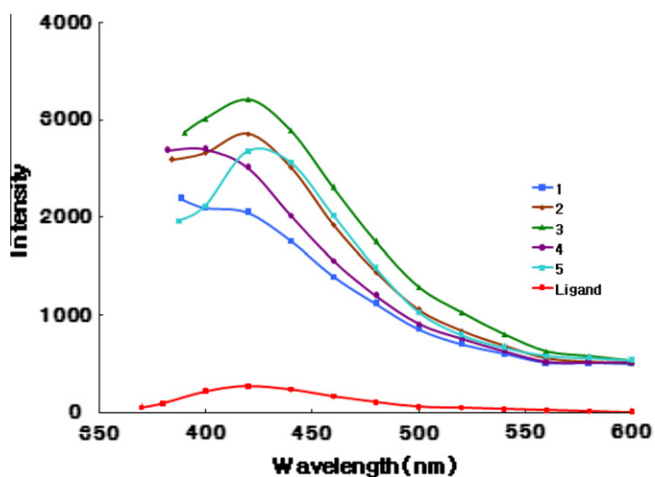**Scheme 3.** Structures of Cd^{II} complexes containing Hdpa or bispicam ligands according to anions.

Fig. 5. Emission spectra of complexes **1–5** and ligand (bispicam) at room temperature.

Table 4
Transesterification of esters by methanol in the presence of compound **5** at 50 °C.[a]

Entry	Substrate	**5** (time/days)[b]
1	4-Nitrophenyl acetate	3
2	Phenyl acetate	6
3	4-Methylphenyl acetate	8
4	4-Nitrophenyl benzoate[c]	0.3
5	4-Chlorophenyl benzoate	2
6	Phenyl benzoate	0.6
7	4-Methylphenyl benzoate	4
8	Vinyl acetate	0.4

[a] All esters were completely converted to the corresponding products, methyl acetate and methyl benzoate. Reaction conditions: esters; 0.05 mmol, catalyst; 1.0 mg, 1.41×10^{-3} mmol for **5**, solvent; methanol (1 mL). See Section 2 for the detailed reaction conditions.
[b] Time necessary for the complete conversion of substrate to product.
[c] The solvent was a mixture of CH$_3$OH/CH$_2$Cl$_2$ (1/1) because of low solubility of substrate in CH$_3$OH.

geometry was obtained. For bromide and iodide, two halide-coordinated [Cd(bispicam)X$_2$] complexes with trigonal bipyramidal geometry were obtained. For nitrate, both a nitrate-coordinated [Cd(bispicam)$_2$(NO$_3$)]$^+$ and a simple [*mer*-Cd(bispicam)$_2$]$^{2+}$ with

three nitrate counter-anions were obtained. These results indicate that anion effects play very important roles for construction of crystal structures and geometrical isomerism. We have also shown that the homogeneous catalyst [Cd(bispicam)$_2$](ClO$_4$)$_2$ (**5**) catalyzed efficiently the transesterification of a variety of esters with
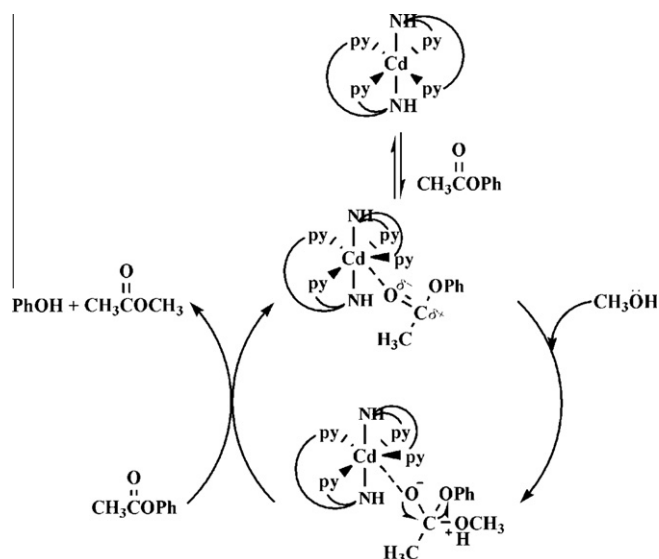
Scheme 4. Proposed reaction mechanism with the saturated complex **5**.
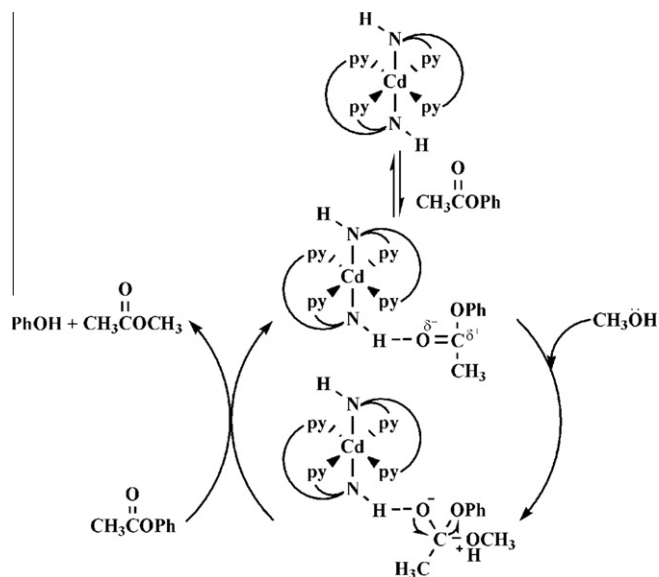
Scheme 5. Another possible mechanism with the saturated complex **5**.

methanol, while rest of the complexes have displayed very slow conversions. Moreover, **1–5** showed the intense emissions at room temperature, which might be due to the intraligand transition of 2,2′-dipicolylamine ligand for **1**, **2**, **3**, and **5**, and to the metal-to-ligand charge transfer (MLCT) and/or ligand-to-metal charge transfer (LMCT) for **4**.

Acknowledgements

Appendix A. Supplementary material

CCDC 806245, 806244, 806246, 806243 and 806242 contains the supplementary crystallographic data for **1**, **2**, **3**, **4** and **5**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via http://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.2012.01.002.

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