Polyhedron 30 (2011) 1555-1564

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Anion effects on the crystal structures of Zn^{II} complexes containing 2,2'-bipyridine: Their photoluminescence and catalytic activities

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ARTICLE INFO

Article history: Received 25 January 2011 Accepted 10 March 2011 Available online 31 March 2011

Keywords: Zn^{II} complexes Photoluminescence 2,2'-Bipyridine Catalyst Transesterification

1. Introduction

Metal–organic coordination polymers are of current interest in the fields of supramolecular chemistry and crystal engineering [1–5]. This interesting topic has shown their intriguing variety of topologies and structural diversity, and their potential applications as functional materials, such as in gas storage [6,7], photoluminescence [8,9], catalysis [10–13], magnetism [14] and molecular sensing [15,16]. Many efforts have been devoted to the study of fundamental structural aspects to understand and control several factors that affect the self-assembly of supramolecular architectures. These factors are the coordination geometry of metal ions [17,18], structure of organic ligands [19–22], the hydrogen bonds[23–32], π – π stacking [4], counter-anions [33–36], pH value [37,38], temperature [39,40], ligand-to-metal ratio [41–44], solvent system [45–47] and template effect [48].

Among them, the anion effect has been realized as a very important role in the self-assembled construction [49]. Many efforts have been devoted to the investigation of new synthetic strategies, with the use of rigid, angular and flexible spacer ligands [50–66]. In our previous attempt to investigate the design and control of the selfassembly of an organic/inorganic supramolecular motif, we have chosen 1,2-*trans*-(4-pyridyl)ethene (bpe) as a rigid ligand [56],

ABSTRACT

Six new structures of Zn^{II} complexes containing 2,2'-bipyridine (2,2'-bpy) ligands have been determined. Halide anions were used as simple coordinating ligands to form a tetrahedral environment around the Zn^{II} ion. Nitrate and benzoate anions were used as chelating ligands to form an octahedral environment. For non-coordinating ClO_4^- and bridging SO_4^{2-} anions, three 2,2'-bpy ligands chelate Zn^{II} to form an octahedral environment, and both ClO_4^- and SO_4^{2-} anions occupy empty positions between the metal cations for charge balance. Polymeric structures of the Zn^{II}-2,2'-bpy complexes are produced by hydrogen bonding. [Zn(2,2'-bpy)(O₂CC₆H₅)₂] catalyzed efficiently the transesterification reaction of esters with methanol under the neutral conditions, while the remaining compounds showed very slow conversions. © 2011 Elsevier Ltd. All rights reserved.

2,6-bis(N'-1,2,4-triazolyl)pyridine (btp) as an angular ligand [11,67,68], 1,3-bis(4-yridyl)propane (bpp) as a flexible ligand [69] and 2,2'-dipyridylamine (Hdpa) as a chelating ligand [70,49]. Especially, the chelating ligand 2,2'-dipyridylamine (Hdpa) showed the formation of mononuclear Zn^{II} complexes by the reaction with zinc salts [35,70], and then these Zn^{II} complexes could be used as building blocks for the construction of polymeric compounds through weak non-classical C/N-H···X and C/N-H···O hydrogen bonding.

POLYHEDRON

As a part of our continued interest (a) for a comparison of the syntheses, structures and reactivities of Zn^{II} complexes with chelating Hdpa ligands, (b) in the aim to fully understand the anion effect of our earlier work, and (c) in order to find efficient catalysts capable of carrying out various catalytic reactions under mild reaction conditions, we have chosen an another chelating ligand, 2,2-bipyridine (2,2'-bpy), with zinc salts containing different counter-anions (Cl⁻, Br⁻, NO₃²⁻, C₆H₅CO₂⁻, ClO₄⁻ or SO₄²⁻). We report here the syntheses, structures and photoluminescence of six new structures of Zn^{II} complexes containing 2,2'-bipyridine ligands, and their catalytic activities for transesterification reactions have been also investigated.

2. Experimental

2.1. Materials

Methanol, ethanol, pentane, methylene chloride, acetone, *para*-substituted phenyl acetate, *para*-substituted phenyl benzoate,



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| Table 1 | | | | |
|------------------|------|-----|-----------|------|
| Crystallographic | data | for | compounds | 1-6. |

| | 1 | 2 | 3 | 4 | 5 | 6 |
|--|--------------------------------|----------------------------|----------------------------|--------------------------------|--------------------------------|--|
| Empirical formula | C10H8Cl2N2Zn | C10H8Br2N2Zn | C20H16N6O6Zn | C24H18N2O4Zn | C30H24Cl2N6O8Zn | C ₃₀ H ₃₉ N ₆ O _{11.5} SZn |
| Formula weight | 292.45 | 381.37 | 501.76 | 463.77 | 732.82 | 765.10 |
| Temperature (K) | 170(2) | 293(2) | 170(2) | 293(2) | 293(2) | 173(2) |
| Wavelength (Å) | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 | 0.71073 |
| Space group | ΡĪ | C2/c | $P2_1/n$ | $P2_1/n$ | ΡĪ | C2/c |
| Unit cell dimensions | | | | | | |
| a (Å) | 7.5521(8) | 10.724(2) | 11.2282(12) | 7.599(4) | 7.9890(16) | 22.6082(16) |
| b (Å) | 8.8244(9) | 14.743(3) | 12.2245(13) | 16.649(9) | 10.979(2) | 13.6295(9) |
| c (Å) | 9.0551(9) | 7.8700(16) | 15.2117(16) | 17.357(10) | 18.666(4) | 24.3347(17) |
| α (°) | 112.488(2) | 90.00 | 90.00 | 90.00 | 100.89(3) | 90.00 |
| β(°) | 94.305(2) | 97.46(3) | 100.854(2) | 101.864(14) | 90.73(3) | 115.0970(10) |
| γ (°) | 95.437(2) | 90.00 | 90.00 | 90.00 | 98.73(3) | 90.00 |
| V (Å ³) | 550.98(10) | 1233.7(4) | 2050.6(4) | 2149(2) | 1587.7(5) | 6790.5(8) |
| Ζ | 2 | 4 | 4 | 4 | 2 | 8 |
| D_{calc} (Mg/m ³) | 1.763 | 2.053 | 1.625 | 1.433 | 1.533 | 1.497 |
| Absorption coefficient(mm ⁻¹) | 2.677 | 8.436 | 1.251 | 1.176 | 1.002 | 0.854 |
| Crystal size (mm) | $0.10 \times 0.08 \times 0.08$ | $0.20\times0.09\times0.08$ | $0.20\times0.15\times0.10$ | $0.15 \times 0.10 \times 0.10$ | $0.25 \times 0.20 \times 0.15$ | $0.20\times0.03\times0.03$ |
| Reflections collected | 3087 | 2976 | 11 037 | 11 819 | 8967 | 18 737 |
| Independent reflections (R_{int}) | 2105 (0.0669) | 1178 (0.0446) | 4011 (0.0599) | 4219 (0.1227) | 6100 (0.0595) | 6662 (0.0825) |
| Data/restraints/parameters | 2105/0/137 | 1178/0/70 | 4011/0/298 | 4219/0/280 | 6100/0/422 | 6662/13/486 |
| Goodness-of-fit on F^2 | 1.037 | 1.007 | 0.892 | 0.818 | 0.927 | 0.955 |
| Final <i>R</i> indices $[I > 2\sigma(I)]$ | $R_1 = 0.0353$, | $R_1 = 0.0625$, | $R_1 = 0.0318$, | $R_1 = 0.0353$, | $R_1 = 0.0610$, | $R_1 = 0.0407$, |
| | $wR_2 = 0.0858$ | $wR_2 = 0.1708$ | $wR_2 = 0.0620$ | $wR_2 = 0.0548$ | $wR_2 = 0.1579$ | $wR_2 = 0.0918$ |
| R indices (all data) | $R_1 = 0.0381$, | $R_1 = 0.0922$, | $R_1 = 0.0439$, | $R_1 = 0.1321$, | $R_1 = 0.0846$, | $R_1 = 0.0548$, |
| | $wR_2 = 0.0864$ | $wR_2 = 0.2273$ | $wR_2 = 0.0633$ | $wR_2 = 0.0639$ | $wR_2 = 0.1655$ | $wR_2 = 0.0946$ |
| Largest difference in peak and hole ($e Å^{-3}$) | 0.948 and -0.809 | 0.974 and -1.200 | 0.343 and -0.525 | 0.230 and -0.212 | 0.787 and -0.895 | 0.529 and -0.825 |



Scheme 1. Structures of Zn^{II} compounds containing 2,2'-bpy ligands.

methylacetate, methylbenzoate, 2,2'-bipyridine, zinc chloride, zinc bromide, zinc sulfate, 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 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. ¹H 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 a 30m 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 $[Zn(2,2'-bpy)X_2]$ (X = Cl for 1, Br for 2)

39.4 mg (0.25 mmol) of 2,2'-bpy ligand were dissolved in 4 mL methylene chloride and carefully layered by 4 mL methanol solution of ZnCl₂ (17.4 mg, 0.125 mmol). Suitable crystals of compound **1** for X-ray analysis were obtained in 3 weeks. The yield was 19 mg (52.0%) for compound **1**. ¹H NMR (DMSO, 400 MHz) *δ*: 8.65 and 8.58 (d, 4H, pyridyl-H), 8.18 and 7.66 (t, 4H, pyridyl-H). IR (KBr) $v(\text{cm}^{-1})$: 3105(s), 2981(m), 1606(s), 1597(s), 1565(s), 1491(s), 1473(s), 1442(s), 1319(s), 1251(s), 1157(s), 1099(s), 1067(s), 1029(m), 905(s), 767(m), 731(s), 650(m). *Anal.* Calc. for C₁₀H₈Cl₂N₂Zn (292.45), **1**: C, 41.07; H, 2.76; N, 9.58. Found: C, 41.42; H, 2.57; N, 9.83%.



Fig. 1. Structure of 1. Displacement ellipsoids are shown at the 50% probability level.



Fig. 2. Structure of 2. Displacement ellipsoids are shown at the 50% probability level.

39.4 mg (0.25 mmol) of 2,2'-bpy ligand were dissolved in 4 mL methylene chloride and carefully layered by 4 mL acetone solution of ZnBr₂·2H₂O (33.0 mg, 0.125 mmol). Suitable crystals of compound **2** for X-ray analysis were obtained in a month. The yield was 21.5 mg (45.2%) for compound **2**. ¹H NMR (DMSO, 400 MHz) δ : 8.60 (d, 4H, pyridyl-H), 8.13 (s, 2H, pyridyl-H), 7.61 (s, 2H, pyridyl-H). IR (KBr) ν (cm⁻¹): 3401(brm), 3073(w), 1647(w), 1596(s), 1472(s), 1440(s), 1315(s), 1251(w), 1158(m), 1100(w), 1062(w),

| able 2 |
|--|
| elected bond lengths (Å) and angles (°) for compounds 1–6 . |

| 1 | | | |
|---|-----------------------|--|--------------------------|
| Zn(1)-N(2) | 2.056(2) | Zn(1)-N(1) | 2.061(2) |
| Zn(1)-Cl(1) | 2.2045(8) | Zn(1)-Cl(2) | 2.2171(8) |
| N(2)-Zn(1)-N(1) | 80.45(9) | N(2)-Zn(1)-Cl(1) | 112.46(7) |
| N(1)-Zn(1)-Cl(1) | 118.58(7) | N(2)-Zn(1)-Cl(2) | 120.04(7) |
| N(1)-Zn(1)-Cl(2) | 102.91(6) | Cl(1)-Zn(1)-Cl(2) | 116.84(3) |
| 2 | | | |
| $\frac{2}{2n(1)-N(1)\#1}$ | 2,038(8) | $Z_{n}(1) - N(1)$ | 2,038(8) |
| Zn(1) - Br(1) # 1 | 2 3504(13) | $Z_n(1) - Br(1)$ | 2,3504(13) |
| N(1)#1-Zn(1)-N(1) | 80.3(4) | N(1)#1-Zn(1)-Br(1)#1 | 107.4(2) |
| N(1) - Zn(1) - Br(1) #1 | 120.71(19) | N(1)#1-Zn(1)-Br(1) | 120.71(19) |
| N(1) - Zn(1) - Br(1) | 107.4(2) | Br(1)#1-Zn(1)-Br(1) | 116.05(8) |
| Symmetry transforma | tions used to g | enerate equivalent atoms: | #1 - x + 1, v. |
| $-z + \frac{1}{2}$ | | , | |
| | | | |
| 3 | | | |
| Zn(1)-N(21) | 2.0647(17) | Zn(1)-N(11) | 2.0724(17) |
| Zn(1) - N(12) | 2.1067(16) | Zn(1) - N(22) | 2.1100(16) |
| Zn(1) - O(32) | 2.1989(16) | Zn(1)-O(33) | 2.2788(15) |
| N(21)-Zn(1)-N(11) | 106.47(7) | N(21)-Zn(1)-N(12) | 101.80(7) |
| N(11)-Zn(1)-N(12) | 79.03(7) | N(21)-Zn(1)-N(22) | 78.86(7) |
| N(11)-Zn(1)-N(22) | 104.15(7) | N(12)-Zn(1)-N(22) | 176.48(7) |
| N(21)-Zn(1)-O(32) | 151.83(6) | N(11)-Zn(1)-O(32) | 100.93(6) |
| N(12)-Zn(1)-O(32) | 89.57(6) | N(22)-Zn(1)-O(32) | 88.34(6) |
| N(21)-Zn(1)-O(33) | 95.89(6) | N(11)-Zn(1)-O(33) | 156.84(6) |
| N(12)-Zn(1)-O(33) | 90.76(6) | N(22)-Zn(1)-O(33) | 85.73(6) |
| O(32)-Zn(1)-O(33) | 57.87(6) | | |
| 4 | | | |
| $\frac{1}{2}$ 7n(1) = O(22) | 2 020(2) | 7n(1) = O(12) | 2.078(2) |
| Zn(1) = N(1) | 2.028(2) | 2n(1) - N(2) | 2.099(3) |
| 2n(1) - O(11) | 2.030(3) | 7n(1) - 0(21) | 2.366(3) |
| $\Omega(22) - 7n(1) - \Omega(12)$ | 14679(10) | O(22) - 7n(1) - N(1) | 106 89(10) |
| O(12) - Zn(1) - N(1) | 98 67(11) | O(22) - Zn(1) - N(2) | 100.00(10) 104.21(10) |
| O(12) - Zn(1) - N(2) | 10157(10) | N(1) - Zn(1) - N(2) | 77 91(14) |
| O(22)-Zn(1)-O(11) | 95.99(10) | O(12) - Zn(1) - O(11) | 60.41(9) |
| N(1)-Zn(1)-O(11) | 157.11(10) | N(2)-Zn(1)-O(11) | 96.33(11) |
| O(22) - Zn(1) - O(21) | 59.43(8) | O(12) - Zn(1) - O(21) | 96.76(9) |
| N(1)-Zn(1)-O(21) | 98.05(12) | N(2)-Zn(1)-O(21) | 161.62(10) |
| O(11)-Zn(1)-O(21) | 93.90(9) | | |
| 5 | | | |
| J $N(11) \ 7n(1)$ | 2 1 1 9 (2) | N(12) = 7n(1) | 2 240(2) |
| N(11) - ZH(1) N(21) - Zn(1) | 2.118(3) | N(12) - 2II(1) N(22) - 7n(1) | 2.240(3) |
| N(21) - ZH(1) N(21) - Zn(1) | 2.207(4) 2.141(2) | N(22) - ZH(1) N(22) - Zh(1) | 2.140(4) 2.110(4) |
| N(31) - ZH(1) N(32) - Zn(1) - N(11) | 2.141(3) 94.56(13) | N(32) - 2n(1) - N(22) | 2.110(4) 96.95(14) |
| $N(11)_7n(1)_N(22)$ | 164 84(14) | N(32) = 2n(1) = N(32) | 76 86(15) |
| N(11) = Zn(1) = N(21) | 101.43(13) | N(32) = 2n(1) = N(31) | 90.80(13) |
| N(32)-Zn(1)-N(21) | 171.01(13) | N(11)-Zn(1)-N(21) | 93.64(14) |
| N(22) = Zn(1) = N(21) | 75.65(15) | N(31)-Zn(1)-N(21) | 97.89(14) |
| N(32) - Zn(1) - N(12) | 102 20(14) | N(11) - Zn(1) - N(12) | 75 83(13) |
| N(22) - Zn(1) - N(12) | 92.06(13) | N(31) - Zn(1) - N(12) | 177.08(13) |
| N(21)-Zn(1)-N(12) | 83.40(13) | | |
| c | | | |
| \mathbf{D} $\mathbf{T}_{\mathbf{D}}(1) = \mathbf{N}(22)$ | 2 120/21 | $7_{\rm p}(1) {\rm N}(21)$ | 2 140(2) |
| LII(1) - IN(22) $T_{P}(1) - IN(12)$ | $2.12\delta(2)$ | $L_{II}(1) = IN(31)$ $T_{II}(1) = N(22)$ | 2.149(2) 2.152(2) |
| LII(1) = IN(12) $T_{D}(1) = N(11)$ | 2.150(2) | $\sum_{i=1}^{2} \frac{1}{2} - \frac{1}{2} \frac{1}{2}$ | 2.152(2) |
| $\Delta H(1) = H(11)$ $H(22) = Z_{D}(1) = H(21)$ | 2.134(2) | $L_{II}(1) = IV(21)$ N(22) = 7n(1) = N(12) | 2.1/3(2) |
| $N(22) = 2\Pi(1) = N(31)$ $N(31) = 2\pi(1) = N(12)$ | 90.24(0) 06.11(9) | $N(22) = 2\Pi(1) = N(12)$ N(22) = 7n(1) = N(22) | 02 00(0) |
| $N(31) - 2\Pi(1) - N(12)$ N(31) - 2n(1) - N(22) | 76 33(9) | $N(22) = 2\Pi(1) = N(32)$ N(12) = 7n(1) = N(22) | 32.33(8) 05.48(8) |
| N(31) - 2H(1) - N(32) N(32) - 7n(1) - N(11) | 0.33(0) 0637(0) | N(12) = 2H(1) = N(32) N(31) = 7n(1) = N(11) | 95.40(0) 06.58(9) |
| N(12) - 2n(1) - N(11) N(12) - 2n(1) - N(11) | 76 52(8) | N(32) - 2n(1) - N(11) N(32) - 7n(1) - N(11) | 168 85(8) |
| N(12) = 2n(1) = N(11) N(22) = 2n(1) = N(21) | 76.32(8) | N(31) - 7n(1) - N(21) | 167 10(8) |
| N(12) - 2n(1) - N(21) | 92 41(8) | N(32) - 7n(1) - N(21) | 93 26(8) |
| N(11) - Zn(1) - N(21) | 94 81(8) | 11(32) -211(1)-11(21) | 55.20(0) |
| | 5(0) | | |

903(w), 774(s), 731(s), 525(s). Anal. Calc. for $C_{10}H_8Br_2N_2Zn$ (381.37), **2**: C, 31.49; H, 2.12; N, 7.35. Found: C, 31.37; H, 2.10; N, 7.57%.

2.4. Synthesis of [Zn(2,2'-bpy)₂(NO₃)](NO₃) (3)

 $38.0 \text{ mg} (0.125 \text{ mmol}) \text{ of } Zn(NO_3)_2 \cdot 6H_2O \text{ and the } 2,2'-bpy ligand (39.4 \text{ mg}, 0.25 \text{ mmol}) were stirred in 2 mL methanol for 6 h at room temperature and carefully layered by 6 mL pentane. Suitable$



Fig. 3. Structure of 3. Displacement ellipsoids are shown at the 50% probability level.

crystals of compound **3** for X-ray analysis were obtained in a week. The yield was 26.9 mg (41.9%) for compound **3**. ¹H NMR (DMSO, 400 MHz) δ : 8.71 and 8.31 (m, 6H, pyridyl-H), 7.75 (m, 2H, pyridyl-H). IR (KBr) ν (cm⁻¹): 3065(w), 1608(m), 1599(m), 1576(w), 1474(s), 1443(s), 1340(s), 1319(s), 1276(s), 1158(m), 1103(w), 1060(w), 1024(s), 969(w), 830(w), 762(s), 734(s), 651(s), 635(s). Anal. Calc. for C₂₀H₁₆N₆O₆Zn (501.76), **3**: C, 47.87; H, 3.22; N, 16.75. Found: C, 47.41; H, 3.18; N, 16.66%.

2.5. Synthesis of $[Zn(2,2'-bpy)(O_2CC_6H_5)_2]$ (4)

38.0 mg (0.125 mmol) of Zn(NO₃)₂·6H₂O and 34.8 mg (0.25 mmol) of ammonium benzoate were dissolved in 4 mL H₂O and carefully layered by an ethanol solution of 2,2'-bpy ligand (39.4 mg, 0.25 mmol). Suitable crystals of compound **4** for X-ray analysis were obtained in 3 weeks. The yield was 16.7 mg (28.7%) for compound **4**. ¹H NMR (pyridine-d₅, 400 MHz) δ: 8.76 (d, 2H, pyridyl-H), 8.70 (d, 2H, pyridyl-H), 8.65 (d, 2H, pyridyl-H), 7.77 (d, 2H, benzoate-H), 7.47 (m, 6H, benzoate-H), 7.25 (d, 2H, benzoate-H). IR (KBr) ν (cm⁻¹): 3072(w), 1595(s), 1538(s), 1474(m), 1442(m), 1401(s), 1317(m), 1252(w), 1172(w), 1074(w), 1025(m), 950(w), 856(m), 769(s), 723(s), 686(s), 633(m), 512(s). *Anal.* Calc. for C₂₄H₁₈N₂O₄Zn (463.77), **4**: C, 62.15; H, 3.92; N, 6.04. Found: C, 61.87; H, 4.21; N, 6.37%.

2.6. Synthesis of [Zn(2,2'-bpy)₃](ClO₄)₂ (5)

47.5 mg (0.125 mmol) of Zn(ClO₄)₂·6H₂O were dissolved in 4 mL H₂O and carefully layered with 4 mL methanol solution of the 2,2'-bpy ligand (39.4 mg, 0.25 mmol). Suitable crystals of compound **5** for X-ray analysis were obtained in 2 months. The yield was 29.3 mg (48.1%) for compound **5**. ¹H NMR (DMSO, 400 MHz) δ : 8.77 and 8.31 (m, 6H, pyridyl-H), 7.75 (m, 2H, pyridyl-H). IR (KBr) *v* (cm⁻¹): 3117(w), 1601(m), 1578(w), 1568(w), 1477(m), 1443(s), 1322(w), 1251(w), 1162(w), 1075(s), 1025(s), 923(m), 903(w), 763(s), 733(s), 652(m), 619(s), 519(s). *Anal.* Calc. for C₃₀H₂₄Cl₂N₆O₈Zn (732.82), **5**: C, 49.17; H, 3.31; N, 11.47. Found: C, 48.92; H, 3.17; N, 11.21%.



Fig. 4. Structure of 4. Displacement ellipsoids are shown at the 50% probability level.

2.7. Synthesis of $[Zn(2,2'-bpy)_3](SO_4)$ (6)

23.2 mg (0.08 mmol) of ZnSO₄ were dissolved in 4 mL methanol and carefully layered with 4 mL acetone solution of the 2,2'-bpy ligand (25.2 mg, 0.16 mmol). Suitable crystals of compound **6** for X-ray analysis were obtained in a week. The yield was 20.7 mg (62.1%) for compound **6**. ¹H NMR (D₂O, 400 MHz) δ : 8.54 (m, 3H, pyridyl-H), 8.27 (m, 3H, pyridyl-H), 7.66 (m, 2H, pyridyl-H). IR (KBr) ν (cm⁻¹): 3212(brm), 3075(m), 1647(w), 1596(m), 1474(s), 1472(w), 1439(m), 1315(w), 1253(w), 1087(s), 1055(s), 018(s), 976(m), 915(m), 763(s), 734(s), 614(s), 521(s). *Anal.* Calc. for C₃₀H₃₉N₆O_{11.5}SZn (765.10), **7**: C, 47.09; H, 5.15; N, 10.99. Found: C, 47.35; H, 5.01; N, 11.23%.

2.8. Catalytic activity of compounds 1-6

Catalytic reaction conditions: The ester (0.05 mmol) was dissolved in methanol (1 mL), and the compounds **1–6** (1.0 mg, 3.42×10^{-3} mmol for **1**, 1.0 mg, 2.62×10^{-3} mmol for **2**, 1.0 mg, 2.00×10^{-3} mmol for **3**, 1.0 mg, 2.16×10^{-3} mmol for **4**, 1.0 mg, 1.36×10^{-3} mmol for **5** and 1.0 mg, 1.31×10^{-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.

2.9. Crystallography

The diffraction data for all six compounds were collected on a Bruker SMART AXS diffractometer equipped with a monochromator in the Mo K α (λ = 0.71073 Å) incident beam. The crystal was mounted on a glass fiber. The CCD data were integrated and scaled using the Bruker-SAINT software package, and the structure was solved and refined using SHEXTL V6.12 [71]. Hydrogen atoms were located in calculated positions. One of ClO₄⁻ anions in **5** has two sets of chlorine atoms with 56%:44% occupancies and was refined isotropically. All hydrogen atoms except hydrogen atoms of water molecules were located in calculated positions. The crystallographic data for compounds **1–6** are listed in Table 1.

3. Results and discussion

In order to understand the anion effects on the construction of crystal structures with the rigid chelating 2,2'-bpy ligand, we synthesized six new compounds, **1–6**. All six structures have been determined by X-ray crystallography. The structures of all six Zn^{II} compounds containing the 2,2'-bpy ligand are shown in Scheme 1.

3.1. Crystal structures of $[Zn(2,2'-bpy)X_2]$ (X = Cl for 1, Br for 2)

The asymmetric unit of **1** consists of a whole molecule, with one 2,2'-bpy ligand chelating the Zn^{II} ion and two halides coordinating to the Zn^{II} ion to form a distorted tetrahedral environment (Fig. 1). The asymmetric unit of **2** consists of half of a molecule, and there is a twofold axis through the C5–C5 (-x + 1, y, -z + 1/2) bond and the Zn^{II} ion (Fig. 2). The geometry of the Zn^{II} ion in **2** is also distorted tetrahedral. The 2,2'-bpy ligands of both compounds are nearly planar. The Zn–N bond distances of both compounds range from 2.038(8) to 2.061(2) Å. The Zn–Cl bond distance is 2.3504(13) Å. The N–Zn–N angles of both compounds range from 80.3(4) to 80.45(9)°, and the X–Zn–X angles are 116.84(3)° for Cl and 116.05(8)° for Br (Table 2). Crystal packing is consolidated by inter-molecular C–H···X non-covalent interactions (Fig. S1 for **1** and S2 for **2**, Table S1).

3.2. Crystal structure of [Zn(2,2'-bpy)₂(NO₃)](NO₃) (**3**)

Two 2,2'-bpy ligands and a nitrate chelate the Zn^{II} ion to form a distorted octahedral environment, and there is a nitrate counter-anion to make the charge balance (Fig. 3). The Zn–N



Fig. 5. (a) Structure of **5.** Displacement ellipsoids are shown at the 50% probability level. (b) The unit cell containing Δ and Λ optical isomers.

bond distances range from 2.0647(17) to 2.1100(16) Å, and Zn– $O_{nitrate}$ distances are 2.1989(16) and 2.2788(15) Å (Table 2). The N–Zn–N angles of 78.86(7)° and 79.03(7)° in this octahedral compound are much smaller than those of tetrahedral compounds **1** and **2** since it has bigger tilting angles between the two pyridyl rings (12.5° and 15.1°). Inter-molecular C–H···O_{nitrate} hydrogen bonding interactions stabilized the crystal structure (Fig. S3, Table S1).

3.3. Crystal structure of $[Zn(2,2'-bpy)(O_2CC_6H_5)_2]$ (4)

Two benzoate ligands and a 2,2'-bpy ligand chelate the Zn^{II} ion to form a distorted octahedral environment (Fig. 4). The 2,2'-bpy ligand is nearly planar. The Zn–N bond distances are 2.098(3) and

2.099(3) Å, and Zn–O_{benzoate} distances range from 2.020(2) to 2.366(3) Å. The N–Zn–N angle is 77.91(4)° (Table 2). The intermolecular C–H···O_{benzoate} hydrogen bonding interactions provide a one-dimensional chain (Fig. S4 and Table S1).

3.4. Synthesis of [*Zn*(2,2'-bpy)₃](*C*lO₄)₂ (**5**) and [*Zn*(2,2'-bpy)₃](SO₄) (**6**)

Both compounds **5** and **6** consist a Zn^{II} ion chelated by three 2,2'-bpy ligands, with two ClO_4^- counter-anions for **5** (Fig. 5(a)) or one SO_4^{2-} anion for **6** (Fig. 6(b)). Both compounds contain Δ and Λ optical isomers in the unit cell, and thus they are optically inactive (Fig. 5(b) for **5** and Fig. 6(b) for **6**). The Zn–N bond distances of both compounds range from 2.110(4) to 2.240(3) Å, and



the N–Zn–N angles range from $75.65(15)^{\circ}$ to $76.86(15)^{\circ}$ (Table 2), which are much smaller than those of the tetrahedral compounds due to the bigger tilting angles between pyridyl rings (5.1° and 8.9°), to form an octahedral geometry with three 2,2′-bpy ligands. There are inter-molecular C–H···O_{perchlorate} hydrogen bonding interactions in **5** (Fig. S5 and Table S1). In **6** there are many water molecules, and hydrogen bonds between those water molecules generate hydrogen-bonded water layers between the molecule layers. The hydrogen-bonded water layers are then connected by

hydrogen bonds between water hydrogen atoms and sulfate oxygen atoms. There are also inter-molecular $C-H\cdots O_{sulfate}$ and $C-H\cdots O_{water}$ hydrogen bonding interactions (Fig. S6 and Table S1).

Hdpa has been used as a chelating ligand to mostly form mononuclear Zn^{II} complexes [35], and then these Zn^{II} complexes can be used as building blocks for one-, two- or three-dimensional structures through weak hydrogen bonding and π - π interactions. To further investigate anion effects for the corresponding Zn^{II} complexes, another chelating ligand, 2,2-bipyridine (2,2'-bpy), has



Scheme 2. Structures according to anions.

Table 3 Transesterification of esters by methanol in the presence of compound 4 at 50 $^{\circ}\text{C.}^{a}$

| Entry | Substrate | 4 (time/days) ^b |
|------------------|--|-----------------------------------|
| 1 | 4-Nitrophenyl acetate | 0.13 |
| 2 | 4-Fluorophenyl acetate | 0.71 |
| 3 | Phenyl acetate | 0.46 |
| 4 | 4-Methylphenyl acetate | 0.38 |
| 5 | 4-Nitrophenyl benzoate ^c | 0.71 |
| 6 | 4-Chlorophenyl benzoate | 1.0 |
| 7 | Phenyl benzoate | 0.75 |
| 8 | 4-Methylphenyl benzoate | 1.0 |
| 9 | Vinyl acetate | 0.13 |
| 6 7 8 9 | 4-Chlorophenyl benzoate Phenyl benzoate 4-Methylphenyl benzoate Vinyl acetate | 1.0 0.75 1.0 0.13 |

^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, 2.16×10^{-3} mmol for **4**, solvent; methanol (1 mL). See Section 2 for the detailed reaction conditions.

^b Time necessary for the complete conversion of substrate to product.

 $^{\rm c}$ The solvent was a mixture of CH₃OH/CH₂Cl₂ (1/1) because of low solubility of the substrate in CH₃OH.



Scheme 3. Plausible transesterification mechanism.

been chosen. Various zinc salts $(ZnX_2 (X = Cl^-, Br^-), Zn(NO_3)_2)$ $Zn(O_2CC_6H_5)_2$, $Zn(ClO_4)_2$ and $Zn(SO_4)$) have been adopted in this system. For each anion, different structures have been obtained in both Zn^{II}-Hdpa and Zn^{II}-2,2'-bpy systems, as shown in Scheme 2. Halide anions were used as simple coordinating ligands for both ligand systems. For halides, the coordination geometry around the Zn^{II} ion is distorted tetrahedral, and hydrogen bond interactions provide polymeric structures. Nitrate and benzoate anions were used as chelating ligands for Zn^{II} ions with very similar structures. For non-coordinating ClO_4^- anions, either three 2,2'-bpy ligands or two Hdpa ligands chelate the Zn^{II} ion along with DMF molecules form an octahedral environment. For bridging SO₄²⁻ anions, Hdpa ligands produced a sulfate-bridged polymeric Zn^{II} complex, while 2,2'-bpy ligands produce a Zn^{II} cation chelated by three 2,2'-bpy ligands. For the Zn^{II} -2,2'-bpy system, both ClO_4^- and SO_4^{2-} anions occupy empty positions between the metal cations for charge balance. Both chelating ligands Hdpa and 2,2'-bpy can provide similar structures for halides, nitrate and benzoate anions. For perchlorate and sulfate, both ligand systems provide different structures, as shown in Scheme 2. Polymeric structures of Zn^{II}-2,2'-bpy complexes can be produced by hydrogen bonding interactions, as shown for the Zn^{II}–Hdpa complexes. These results confirm that inter-molecular hydrogen bonding interactions, as well as anion effects, also play a very important role in the construction of crystal structures in both the Zn^{II}-Hdpa and Zn^{II}-2,2'-bpy systems.

3.5. Catalytic transesterification reactions by compounds 1-6

As part of our efforts to develop transesterification catalysts based on metal ions that are not redox active, we have previously investigated the catalytic transesterification of several zinc complexes containing a chelating Hdpa ligand at room temperature under mild conditions. Importantly, they have shown efficient catalytic activities on the transesterification reaction of a range of esters with methanol [35,70]. Our interest for a comparison of the reactivities of compounds **1–6** with Zn^{II} complexes having a chelating Hdpa ligand led us to attempt the transesterification reaction using compounds **1–6**. Treatment of 4-nitrophenyl acetate and methanol in the presence of **1–6** at 50 °C produced methyl acetate quantitatively within 5 days for **1**, 8 days for **2**, 7 days for **3**, 0.13 days for **4**, 8 days for **5** and 11 days for **6**, under neutral conditions (Eq. (1)). Only a little transesterification occurred without catalysts **1–6** over the same time period¹

$$O_2 N - \bigcirc O_{CCH_3} + H_{OCH_3} \xrightarrow{\text{catalysts 1-6}} O_2 N - \bigcirc O_{H} + CH_3 \xrightarrow{O} O_{CCH_3}$$
(1)

Compound **4**, with two labile benzoate ligands, was most efficient and the reactivity of **4** is the second best among the catalytic systems reported previously in Zn-containing coordination and polymeric compounds, to the best of our knowledge [35,49,68-70]. With these promising results, we have examined further the transesterification of other esters by **4** and the results are shown in Table 3. The substrates *p*-nitrophenyl acetate and benzoate, with an electron-withdrawing substituent at the *para*-position, undergo faster transesterification (entries 1 and 5). Also, *para*-substituted phenyl acetate groups (entries 1–3) display better reactivity than *para*-substituted phenyl benzoate groups (entries 4–8). Moreover, vinyl acetate was converted effectively to the product methyl acetate within 0.13 days by **4**. These results suggest that compound **4** could be an efficient catalyst for ester synthesis by transesterification.

As it has been proposed that the Lewis acidity of the metal center may be important in catalytic transesterification [72,73], a possible transesterification mechanism in this catalyst system could be proposed, as shown in Scheme 3. In the first step, the substrate phenyl acetate substitutes a labile benzoate ligand to give the adduct **A**. Then, the nucleophile methanol attacks the carbon atom of carbonyl moiety of the adduct to produce the product methyl acetate. Further detailed mechanistic studies are currently under investigation.

3.6. Photoluminescence property

Previous studies have shown that coordination polymers containing cadmium and zinc exhibit photoluminescent properties [74–76]. Therefore, the emission spectra of Zn^{II} complexes **1–6**, together with that of the ligand 2,2'-bpy, were measured in the solid state at room temperature (see Fig. 7), based on their UV–Vis spectra (Fig. S7). Emissions of compounds **1**, **3**, **4**, **5** and **6** were observed

¹ We have carried out some control experiments for a comparison of the reactivity of compound **4** and zinc salts like ZnCl_2 , ZnBr_2 , and zinc acetate. Treatment of phenyl acetate and methanol in the presence of zinc salts at 50 °C produced methyl acetate quantitatively within 6 days for ZnCl_2 , 7 days for ZnBr_2 , 3 days for zinc acetate, respectively, indicating that compound **4** (0.46 days) shows much more efficient reactivity than the zinc salts.



Fig. 7. (a) Emission spectra of complexes 1-6 and the ligand 2,2'-bpy at room temperature. (b) Expanded emission spectra of complex 2 and the ligand 2,2'-bpy.

at 349 nm (λ_{ex} = 230 nm) for **1**, 400–422 nm (λ_{ex} = 272 nm) for **3**, 350 nm (λ_{ex} = 272 nm) for **4**, 344 nm (λ_{ex} = 272 nm) for **5**, and 366 nm (λ_{ex} = 272 nm) for **6**, but relatively very weak luminescences were observed under the same experimental conditions for 2 $(360 \text{ nm}, \lambda_{ex} = 272 \text{ nm})$ and 2,2-bpy $(398 \text{ nm}, \lambda_{ex} = 330 \text{ nm})$ (see inset in Fig. 7 for 2 and ligand 2,2-bpy). The emission bands of complexes 1, 4, 5 and 6 are blue-shifted compared to the corresponding ligand (398 nm for 2,2'-bpy), which indicates that the emission peaks of 1, 4, 5 and 6 may be due to a metal-to-ligand charge transfer (MLCT) and/or ligand-to-metal charge transfer (LMCT). Such an emission of complex 3 can be tentatively assigned to the intraligand transition of the 2,2-bpy ligand, since a similar emission was observed for the ligand. In addition, it is noteworthy that 1, 3, 4, 5 and 6 show intense emissions at room temperature, suggesting that they may be good candidates for a potential hybrid inorganic-organic photoactive material [76].

Acknowledgments

Financial support from the Korean Science and Engineering Foundation (R01-2008-000-20704-0 and 2009-0074066), Converging Research Center Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2009-0082832), and SRC program of NRF through the Center for Intelligent Nano-Bio Materials at Ewha Womans University (20090063004) is gratefully acknowledged.

Appendix A. Supplementary data

CCDC 802853, 802852, 802855, 802857, 802854 and 802856 contain the supplementary crystallographic data for **1**, **2**, **3**, **4**, **5** and **6**. These data can be obtained free of charge via http:// www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223–336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2011.03.040.

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