

Synthesis and Crystal Structures of Di-nuclear Zinc(II) Diphenate Complexes with 1,10-Phenanthroline and 2,2'-Bipyridine

Bon Kweon Koo

Department of Chemistry, Catholic University of Daegu, Gyeongsbuk 712-702, Korea. E-mail: bkkoo@cu.ac.kr
Received May 12, 2011, Accepted June 24, 2011

Two new Zn(II) complexes, $[\text{Zn}_2(\text{dpa})_2(\text{phen})_2(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ (**1**) (dpa = diphenate, phen = 1,10-phenanthroline) and $[\text{Zn}_2(\text{dpa})_2(\text{bpy})_2(\text{H}_2\text{O})_2]$ (**2**) (bpy = 2,2'-bipyridine) have been synthesized and characterized by elemental analysis, infrared spectroscopy, thermogravimetric analysis, and single crystal X-ray diffraction. The X-ray analysis reveals that the structures of **1** and **2** are dinuclear zinc(II) complexes bridged by dpa dianions, respectively. The zinc ions in **1** exhibit a distorted square pyramidal environments, while the zinc ions in **2** exhibit a trigonal bipyramid geometry. In each complex, the dpa ligand is coordinated to zinc ions as a bis-monodentate.

Key Words : Dinuclear zinc(II) complexes, Diphenate, Crystal structure, Thermal properties

Introduction

Recently much attention has been paid to design and synthesis of metal-organic hybrid materials with fascinating network topologies¹⁻³ and potential applications as functional materials.⁴⁻⁸ The most commonly used strategy for designing such materials relies on the utilization of multi-dentate N- or O-donor ligands which have the capacity to bridge between metal centers to form polymeric structures. Multi-carboxylate ligands, especially dicarboxylate ligands, have been extensively used to form metal-organic frameworks (MOF), in which rigid multi-carboxylate ligands, such as 1,2-benzene dicarboxylate, 1,3-benzenedicarboxylate, 1,4-benzenedicarboxylate, 1,2,4-benzene tricarboxylate, and 1,3,5-benzene tricarboxylate, have been used as a building block to construct some porous coordination frameworks.⁹⁻¹¹ In contrast to the rigid aromatic multi-carboxylate anions, the aliphatic α,ω -dicarboxylate ligands as important flexible spacer ligands due to their conformational and coordination versatility tend to bridge transition metal ions to form coordination polymers with a variety of interesting structures.¹²⁻¹⁴

Diphenic acid is a useful source possessing several novel features besides its metrics of aromatic dicarboxylate ligands. It has 2,2'-positioned carboxyl groups with the steric hindrance, and two phenyl rings are not coplanar. The carboxyl groups can partly or entirely deprotonated, which makes it possible to coordinating with metal ion or forming hydrogen bonding interactions. Many frameworks constructed by dpa^{2-} or Hdpa^- with transition metal ions or rare earth ions have been reported, mainly using hydrothermal synthetic method.¹⁵⁻²⁰ Also, the auxiliary ligands, such as 1,10-phenanthroline or 2,2'-bipyridine, have obvious great effect on the structures of complexes. The combination of the metal ion and above-mentioned two types of bridging and auxiliary ligands can generate some unique structural motifs, which cannot be obtained only through one type of

ligands.

In view of these factors, we explored the self-assembly of Zn(II) ion, H_2dpa , and phen/bpy under hydrothermal conditions, and obtained two crystalline complexes: $[\text{Zn}_2(\text{dpa})_2(\text{phen})_2(\text{H}_2\text{O})_2]\cdot\text{H}_2\text{O}$ (**1**) and $[\text{Zn}_2(\text{dpa})_2(\text{bpy})_2(\text{H}_2\text{O})_2]$ (**2**). These discrete units were further extended into supramolecular framework by hydrogen bonds and π - π stacking interactions. Herein, we report the synthesis, crystal structures, and thermal properties of two new zinc(II) complexes.

Experimental

Chemicals and Measurements. All chemicals are commercially available and were used as received without further purification. Elemental analyses (CHN) were performed on a Vario EL EA-Elementar Analyzer. Infrared spectra were recorded in the range from 4000 to 400 cm^{-1} on a Mattson Polaris FT-IR Spectrophotometer using KBr pellets. Thermogravimetric (TG) and differential thermal analysis (DTA) were performed on a Shimadzu DTG-60 instrument with a heating rate of 10 $^\circ\text{C}\cdot\text{min}^{-1}$.

Preparation of $[\text{Zn}_2(\text{dpa})_2(\text{phen})_2(\text{H}_2\text{O})_2](\text{H}_2\text{O})$ (1**).** A mixture of $\text{Zn}(\text{OAc})_2\cdot 2\text{H}_2\text{O}$ (0.033 g, 0.15 mmol), H_2dpa (0.037 g, 0.15 mmol), phen (0.025 g, 0.15 mmol), NaOH (0.1 mL, 0.65 M), 10 mL H_2O and 1 mL ethanol was placed in a 23 mL Teflon-lined stainless steel autoclave, and the vessel was heated to 120 $^\circ\text{C}$ for 3 days. The resulting colorless block crystals were filtered off and washed with water and then dried at room temperature. Yield 75% (0.059 g) based on Zn. Anal. Calcd. for $\text{C}_{52}\text{H}_{38}\text{N}_4\text{O}_{11}\text{Zn}_2$: C, 60.89; H, 3.73; N, 5.46. Found: C, 61.05; H, 3.96; N, 5.46%. IR (KBr pellet, cm^{-1}): 3589(w), 3476(w), 3060(w), 1615(s), 1564(m), 1519(m), 1429(m), 1356(s), 1147(m), 847(m), 809(m), 780(m), 724(m).

Preparation of $[\text{Zn}_2(\text{dpa})_2(\text{bpy})_2(\text{H}_2\text{O})_2]$ (2**).** The compound was prepared similarly by the method described above for the preparation of **1**, with use of 2,2'-bpy instead

Table 1. Crystal data and structure refinement for complexes **1** and **2**

Complex	1	2
Empirical formula	C ₅₂ H ₃₈ N ₄ O ₁₁ Zn ₂	C ₄₈ H ₃₆ N ₄ O ₁₀ Zn ₂
Formula weight	1025.61	959.55
T (K)	200(2)	200(2)
λ (Å)	0.71073	0.71073
Crystal system	Triclinic	monoclinic
Space group	P-1	P2(1)/c
<i>a</i> (Å)	8.1206(6)	10.9366(7)
<i>b</i> (Å)	11.7188(10)	9.4322(6)
<i>c</i> (Å)	12.6303(10)	20.5141(14)
α (°)	106.947(2)	
β (°)	104.728(2)	104.590(2)
γ (°)	97.638(2)	
<i>V</i> (Å ³)	1083.78(15)	2047.9(2)
Z	1	2
μ (mm ⁻¹)	1.179	1.240
<i>F</i> (000)	524	984
θ (°)	1.77 to 28.31	1.92 to 28.29
Absorption correction	multi-scan T _{min} =0.822, T _{max} =0.924	multi-scan T _{min} =0.796, T _{max} =0.904
Limiting indices	-8 ≤ <i>h</i> ≤ 10, -15 ≤ <i>k</i> ≤ 13, -16 ≤ <i>l</i> ≤ 16	-13 ≤ <i>h</i> ≤ 14, -12 ≤ <i>k</i> ≤ 10, -27 ≤ <i>l</i> ≤ 27
Reflections collected	8107	14861
Independent reflections	5308 [R(int)=0.0314]	5086 [R(int)=0.0785]
Observed reflections [I ≥ 2σ(I)]	3832	2924
Goodness-of-fit on <i>F</i> ²	1.149	1.096
<i>R</i> ₁ [I ≥ 2σ(I)]	0.0676	0.0571
<i>wR</i> ₂ [I ≥ 2σ(I)]	0.1274	0.0888
<i>R</i> ₁	0.1191	0.1296
<i>wR</i> ₂	0.1962	0.1352
Largest peak and hole (eÅ ⁻³)	1.778 and -2.569	1.091 and -1.801

of phen. Yield 57% (0.042 g) based on Zn. Anal. Calcd. for C₄₈H₃₆N₄O₁₀Zn₂: C, 60.08; H, 3.78; N, 5.84. Found: C, 60.03; H, 4.01; N, 5.82%. IR (KBr pellet, cm⁻¹): 3680(m), 2973(s), 1631(m), 1552(m), 1442(m), 1390(m), 1334(m), 1056(s), 1033(s), 1013(m), 774(m), 752(m).

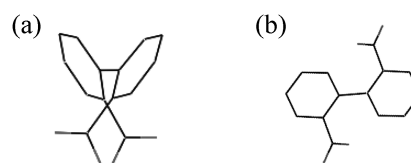
X-ray Structure Determination. Single crystals of **1** and **2** were obtained by the method described in the above procedures. Structural measurement for the two complexes were performed on a Bruker SMART APEX CCD diffractometer using graphite monochromatized Mo-K α radiation ($\lambda = 0.71073$ Å) at the Korea Basic Science Institute. A multi-scan absorption correction was applied using the SADABS program.²¹ The structures were solved by direct method and refined on *F*² by full-matrix least-squares procedures using the SHELXTL programs.²² All non-hydrogen atoms were refined using anisotropic thermal parameters. CH hydrogen atoms were included in the structure factor calculation at idealized positions by using a riding model, but not refined. Images were created with the ORTEP²³ or DIAMOND pro-

gram.²⁴ The crystallographic data for complexes **1** and **2** are listed in Table 1

Results and Discussion

Description of the Structures. The structure of **1** consists of dinuclear species, [Zn₂(dpa)₂(phen)₂(H₂O)₂] and one lattice water (Fig. 1(a)). In the dinuclear unit, each zinc(II) ion exhibits a distorted square pyramidal environments with $\tau = 0.43$ [$\tau = |\beta - \alpha|/60^\circ$], where β and α are the two largest angles around the central atom; $\tau = 0$ and 1 for the perfect square pyramidal and trigonal bipyramidal geometries, respectively.^{25,26} Two nitrogen atoms from one chelating ligand phen and two oxygen atoms from one dpa and one coordinated water define the basal plane, where the apical position is occupied by an another dpa ligand oxygen. The basal plane (N1N2O1O5) is nearly planar (mean deviation 0.242(5) Å) and the Zn1 is displaced by 0.537(1) Å from the plane toward O3ⁱ. The structural data (Table 2) are in agreement with those of the zinc(II) complexes which exhibit the similar geometry.²⁷⁻²⁹

The dpa ligand adopts bis-monodentate coordination mode and shows *cis*-configuration (see Scheme 1(a)). Two dpa ligands link two Zn(II) atoms (Zn1 \cdots Zn1ⁱ = 4.719(1) Å), forming a cyclic dimer.



Scheme 1. The coordination modes of dpa ligand.

Two planes [C20–C25 and C14–C19] in dpa are nearly planar with mean deviation of 0.007(7) Å, respectively, the dihedral angle between the two planes being 81.8(2)°. The O1–C13 bond length is somewhat longer than the O2–C13 as expected from oxygen O1 involved in coordination (Table 2). The phen molecules are also nearly planar [the largest deviation of atoms from the mean plane is C2 atom, -0.078(8) Å], the dihedral angles between the mean planes of three planes (C1–C4C12N1, C4–C7C11C12, and C7–C11N2) being 1.6(2)–4.1(2)°. In the complex, two phen ligands are *trans* oriented to each other. The intra-ring C–N [mean value: 1.333(8) Å] and C–C [mean value; 1.401(9) Å for phen and 1.411(9) Å for dpa] bond distances are as expected.^{30,31}

The dinuclear units are further stabilized by the intramolecular hydrogen bonds involving the coordinated water molecules and carboxylate oxygen atoms (coordinated) [O5–H5 \cdots O3] (Fig. 1(b)). In addition, intermolecular hydrogen bonds (C–H \cdots O) are also observed between the phen molecules and the oxygen atoms of the carboxylates and between dpa ligands. The hydrogen bonds (C6–H6 \cdots O2 and C8–H8 \cdots O2) between phen molecule and carboxylate oxygen form 1D chain network along *c*-axis, which is further

Table 2. Selected bond lengths (Å) and angles (°) for complex **1** and **2**

Complex 1			
Zn1–O1	1.970(4)	Zn1–O3 ⁱ	2.039(4)
Zn1–O5	2.113(4)	Zn1–N1	2.115(5)
Zn1–N2	2.142(5)	O1–C13	1.290(7)
O2–C13	1.237(7)	O3–C26	1.287(8)
O4–C26	1.220(8)		
O3 ⁱ –Zn1–O1	95.36(18)	O3 ⁱ –Zn1–O5	95.58(18)
O1–Zn1–O5	88.81(17)	O3 ⁱ –Zn1–N1	102.13(19)
O1–Zn1–N1	162.51(18)	O5–Zn1–N1	89.93(19)
O3 ⁱ –Zn1–N2	127.9(2)	O1–Zn1–N2	91.09(19)
O5–Zn1–N2	136.27(19)	N1–Zn1–N2	77.9(2)
O2–C13–O1	123.0(5)	O4–C26–O3	124.1(6)

Symmetry codes: i) 1-x, 1-y, 2-z

Complex 2			
Zn1–O1	1.981(3)	Zn1–O3 ⁱ	1.999(3)
Zn1–O5	2.119(4)	Zn1–N1	2.155(4)
Zn1–N2	2.114(4)	O1–C11	1.288(6)
O2–C11	1.226(6)	O3–C24	1.272(6)
O4–C24	1.257(6)		
O3 ⁱ –Zn1–O1	121.54(14)	O3 ⁱ –Zn1–O5	86.64(14)
O1–Zn1–O5	95.82(14)	O3 ⁱ –Zn1–N1	94.16(15)
O1–Zn1–N1	95.34(15)	O5–Zn1–N1	166.37(15)
O3 ⁱ –Zn1–N2	115.28(15)	O1–Zn1–N2	123.07(15)
O5–Zn1–N2	90.48(15)	N1–Zn1–N2	76.85(17)
O2–C11–O1	123.1(5)	O4–C24–O3	124.0(5)

Symmetry codes: i) 1-x, 1-y, -z

stabilized by the inter-phen ring π - π stacking (interplanar distance is 3.665 Å) (Fig. 1(b)).³² The hydrogen bond between dpa ligands, C24–H24 \cdots O4 links the dimers into 1D chain along b-axis, to form 2D network (bc-plane). While, the hydrogen bonds, C2–H2 \cdots O3 and C16–H16 \cdots O2 bring the formation of 3D supramolecular network (Fig. 1(c)). The details of hydrogen bonds are listed in Table 3.

Complex **2** is also composed of a dimer. The asymmetric unit of **2** consists of a Zn(II) ion, one dpa ligand, one bpy ligand and one water molecule. Each Zn(II) ion is located in an distorted trigonal bipyramidal geometry ($\tau = 0.72$) in which the equatorial positions are occupied by the O1, O3, N2 and the axial positions by O5 and N1 with the O5–Zn1–N1 angle of 166.37(15)° showing the large deviation from an ideal value of 180° (Fig. 2(a)). The average Zn–N bond length is 2.135(4) Å, longer than the average Zn–O distance (2.033(3) Å) (Table 2). These structural data are in agreement with those of the zinc(II) complex, Zn₂(DPA)₂(mbix)·(H₂O) (mbix = 1,3-bis(imidazol-1-ylmethyl)benzene)³³ which exhibit the similar formula. The zinc(II) ions bridged by the dpa in a bis-monodentate fashion are separated by 4.544(1) Å. Each Zn(II) ion is slightly displaced (0.039(1) Å) from the equatorial plane toward the O5. Other structural data are also similar to the values of complex **1**.

The dinuclear units are interconnected through intra- and inter-molecular hydrogen bonds and π - π stacking interaction.

Table 3. Parameters (Å, °) for hydrogen-bonding interaction of complex **1** and **2**

Donor–H \cdots acceptor	D–H	H \cdots A	D \cdots A	D–H \cdots A
Complex 1				
O5–H5A \cdots O3	0.98	2.21	3.08(1)	147.9
C2–H2 \cdots O3 ⁱ	0.95	2.83	3.57(1)	135.3
C6–H6 \cdots O2 ⁱⁱ	0.95	2.99	3.71(1)	132.8
C8–H8 \cdots O2 ⁱⁱ	0.95	2.33	3.20(1)	152.9
C16–H16 \cdots O2 ⁱⁱⁱ	0.95	2.57	3.56(1)	140.9
C24–H24 \cdots O4 ^{iv}	0.95	2.48	3.32(1)	146.6
Symmetry codes: i) 2-x, 1-y, 2-z; ii) 1-x, 1-y, 1-z; iii) -1+x, y, z; iv) 1-x, -y, 2-z				
Complex 2				
O5–H5B \cdots O1 ⁱ	0.98	1.80	2.73(1)	156.6
C1–H1 \cdots O4 ⁱ	0.95	2.48	3.17(1)	129.9
C2–H2 \cdots O5 ⁱⁱⁱ	0.95	2.62	3.47(1)	149.0
C4–H4 \cdots O2 ⁱⁱ	0.95	2.33	3.10(1)	137.8
C7–H7 \cdots O4 ⁱⁱ	0.95	2.95	3.57(1)	123.7
C8–H8 \cdots O4 ⁱⁱ	0.95	2.89	3.54(1)	126.3
C16–H16 \cdots O3 ^{iv}	0.95	2.84	3.50(1)	127.2
Symmetry codes: i) 1-x, 1-y, -z; ii) 1-x, -1/2+y, 1/2-z; iii) x, -1-y, z; iv) 2-x, 1-y, -z.				

There is intramolecular hydrogen bonds involving the coordinated water molecules and carboxylate oxygen atoms [O5–H5 \cdots O1]. While, the dimeric units are interconnected through intermolecular hydrogen bonds between the bpy molecules and oxygen atoms of the carboxylates (uncoordinated) (C1–H1 \cdots O4, C4–H4 \cdots O2, C7–H7 \cdots O4, C8–H8 \cdots O4) to give 1D chain along the c-axis (Fig. 2(b)). The 1D chain is further stabilized by inter-phen π - π stacking interactions (interplanar distance (mean value) = 3.838 Å).³² The hydrogen bondings between the dpa ligands (C16–H16 \cdots O3) link these 1D chains together to form 2D layer. The 2D network structure is also connected through hydrogen bonding (C2–H2 \cdots O5) to give further extended 3D network structure (Fig. 2(c)). The D \cdots A bond distance and D–H \cdots A angles are listed in Table 3.

IR Spectra. The IR spectra of the complexes **1** and **2** exhibit characteristic bands for the carboxylic groups of dicarboxylates. The strong bands assigned to asymmetric stretching vibration $\nu_{as}(\text{COO}^-)$ and symmetric stretching vibration $\nu_s(\text{COO}^-)$ of the carboxylate groups are observed in the expected regions at 1615 and 1356 cm^{-1} for **1**, and 1631 and 1334 cm^{-1} for **2**, respectively.^{34,35} The separations ($\Delta\nu = 259$ for **1** and 296 cm^{-1} for **2**) between $\nu_{as}(\text{COO}^-)$ and $\nu_s(\text{COO}^-)$ indicate the presence of monodentate mode in dpa, which are consistent with their crystal structures.^{36,37} The IR spectra also show the bands at 3589 (3680 for **2**) and 3476 cm^{-1} corresponding to the vibration absorption of coordinated water and lattice water, respectively.^{38,39}

Thermal Analysis. TG–DTA curves have been obtained in flowing N₂ atmosphere for crystalline samples of **1** and **2** in the temperature range of 30–800 °C with a rate of 10 °C min⁻¹ (Fig. 3). The TG curves are divided into three stages.

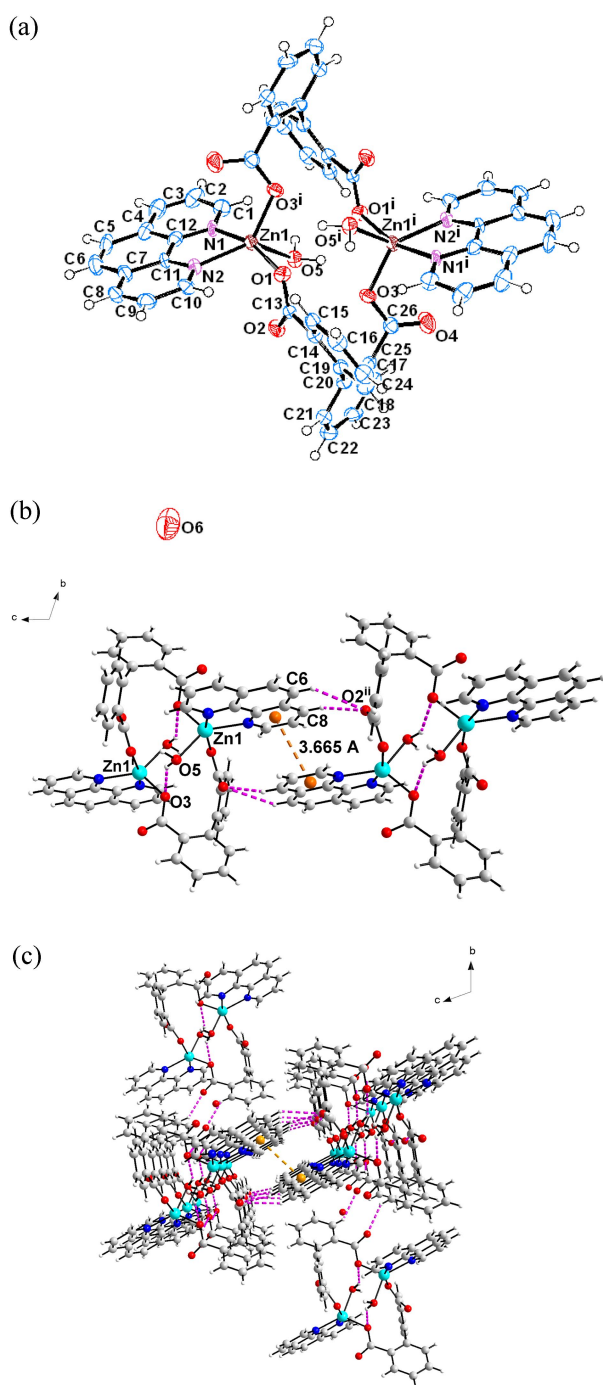


Figure 1. (a) Coordination environment of complex **1**, showing 50% thermal ellipsoids and the atomic labeling. (b) 1D chain structure of complex **1** through hydrogen bonding and inter-phen π - π Interactions (along c-axis). (c) Packing diagram of complex **1** viewed along a-axis. Symmetry codes: i) 1-x, 1-y, 2-z; ii) 1-x, 1-y, 1-z.

For complex **1**, the first weight loss of 5.67% between 97 and 174 °C with a sharp endothermic peak at 173 °C corresponds to the loss of one lattice and two coordinated water molecules per formula unit (calc. 5.27%). Upon further heating up to 560 °C, the anhydrous compositions show two indistinct weight loss stages with 80.27% in total

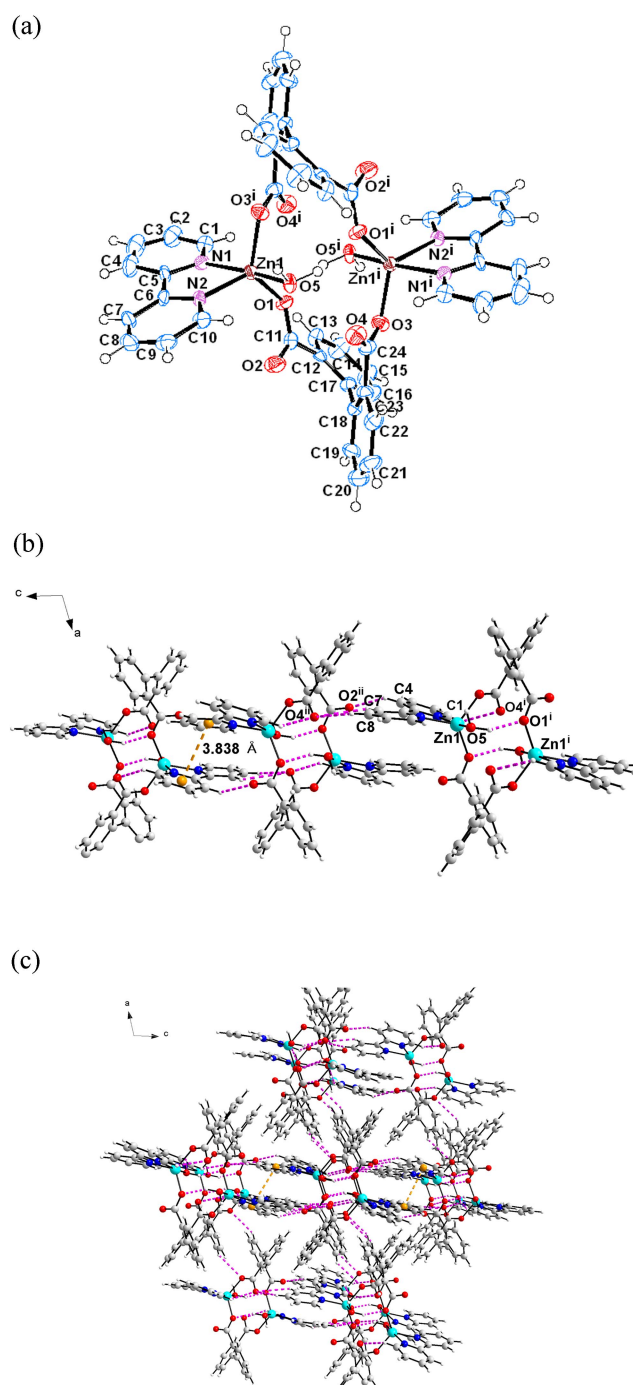


Figure 2. (a) Coordination environment of complex **2**, showing 50% thermal ellipsoids and the atomic labeling. (b) 1D chain structure of complex **2** through hydrogen bonding and inter-phen π - π Interactions (along c-axis). (c) Packing diagram of complex **2** viewed along b-axis. Symmetry codes: i) 1-x, 1-y, -z; ii) 1-x, -1/2+y, 1/2-z.

(calc. 81.98%) corresponding to the decomposition of organic ligands. The final decomposed product presumably is attributed to ZnO (found 14.05%. calc. 15.88%). While, complex **2** shows the first weight loss of 3.90% (calc. 3.75%) from 136 to 168 °C with an endothermic peak at 163 °C, which corresponds to the release of coordinated water

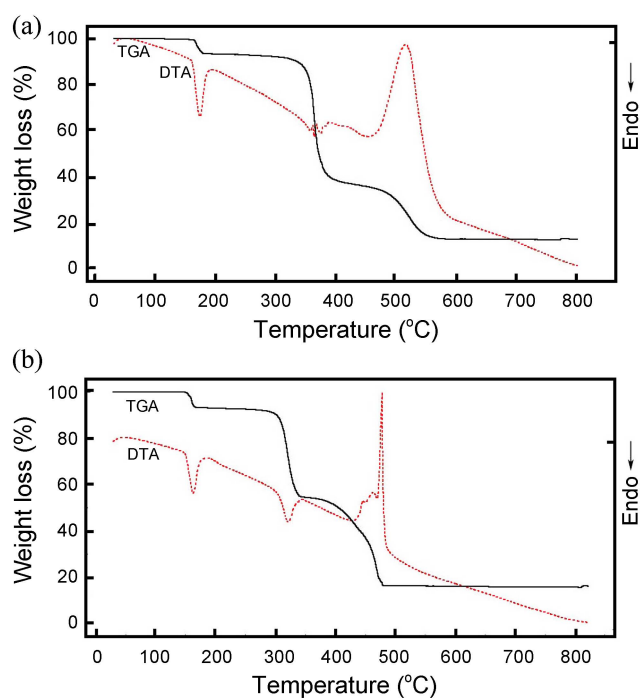


Figure 3. TG curves of complex 1 (a) and 2 (b).

molecule. Over 168–481 °C, the sample loses the additional weight of 79.94% (calc. 82.61%) corresponding to the decomposition of organic ligands in two steps overlapping to each other. These weight losses are accompanied by an endothermic and an exothermic effect on the DTA curve with maximum at 322 and 478 °C, respectively. The remaining weight corresponds to the formation of ZnO (obsd. 16.14%, calc. 16.96%).

Conclusion

We have synthesized two zinc(II) complexes **1** and **2** from the reaction mixture of $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, H_2dpa , phen/bpy, NaOH, H_2O , and ethanol in the mole ratio 1.00:1.00:1.00:4.33:370.37:10.39 at 120 °C by the hydrothermal reaction. The structures of **1** and **2** are dinuclear zinc(II) complexes bridged by dpa dianions, respectively. The zinc ions in **1** exhibit a distorted square pyramidal environments, while the zinc ions in **2** exhibit a trigonal bipyramid geometry. In each complex, the dpa ligand is coordinated to zinc ions as a bis-monodentate. The dinuclear units of **1** and **2** are interconnected through intermolecular hydrogen bonds between the phen/bpy molecules and oxygen atoms of the carboxylates (coordinated and uncoordinated) to give 1D chain. In addition, both complexes show further extended 3D supramolecular network by the π - π stacking as well as hydrogen bonding interaction. Although many interesting polymeric complexes containing the multi-carboxylate ligands have been reported, uncharacterized polymers were often obtained in hydrothermal reactions. Thus, the development of synthetic routes to the systems containing dicarboxylate is still required for the rational design and synthesis.

Supplementary Materials. Crystallographic data in CIF format have been deposited with the Cambridge Structural Database CCDC 825055 for **1** and 825056 for **2**, respectively. These data can be obtained free of charge at 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; E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments. This work was supported by the 2011 Research Fund of Catholic University of Daegu. The author also acknowledges the Korea Basic Science Institute for providing the crystal structure results.

References

- Batten, S. R.; Robson, R. *Angew. Chem. Int. Ed.* **1998**, *37*, 1460.
- Hagrman, P. J.; Hagrman, D.; Zubieta, J. *Angew. Chem. Int. Ed.* **1999**, *38*, 2638.
- Carlucci, L.; Ciani, G.; Proserpio, D. *Coord. Chem. Rev.* **2003**, *246*, 247.
- Jose, S.-V.; Mota, A. J.; Aouryaghal, H.; Cano, J.; Rodriguez-Dieguez, A.; Luneau, D.; Colacio, E. *Inorg. Chem.* **2008**, *47*, 8143.
- Liu, Y.; Hou, H.; Chen, Q.; Fan, Y. *Cryst. Growth Des.* **2008**, *8*, 1435.
- Takaya, J.; Iwasawa, N. *J. Am. Chem. Soc.* **2008**, *130*, 15254.
- Spencer, E. C.; Howard, J. A. K.; McIntyre, G. J.; Rowsell, J. L. C.; Yaghi, O. M. *Chem. Commun.* **2006**, 278.
- Ruben, M.; Rojo, J.; Romero-Salguero, F. J.; Uppadine, L. H.; Lehn, J.-M. *Angew. Chem. Int. Ed.* **2004**, *43*, 3644.
- Cui, Y.; Lee, S. J.; Lin, W. *J. Am. Chem. Soc.* **2003**, *125*, 6014.
- Horikoshi, R.; Mochida, T.; Moriyama, H. *Inorg. Chem.* **2002**, *41*, 3017.
- Li, X.; Cao, R.; Sun, Y. Q.; Shi, Q.; Yuan, D. Q.; Sun, D. F.; Bi, W. H.; Hong, M. C. *Cryst. Growth Des.* **2004**, *4*, 225.
- Kim, Y.; Jung, D. Y. *Inorg. Chem.* **2000**, *39*, 1470.
- Bakalbassis, E. G.; Michailides, M. K. A.; Mrozinski, J.; Raptopoulou, C.; Skoulika, S.; Terzis, A.; Tsaousis, D. *J. J. Chem. Soc., Dalton Trans.* **2001**, *6*, 850.
- Mukherjee, P. S.; Konar, S.; Zangrando, E.; Mallah, T.; Ribas, J.; Chaudhuri, N. R. *Inorg. Chem.* **2003**, *42*, 2695.
- Shi, Q.; Sun, Y.; Sheng, L.; Ma, K.; Cai, X.; Liu, D. *Inorg. Chim. Acta* **2009**, *362*, 4167.
- Karle, I. L.; Venkateswarlu, P.; Nagaraj, R.; Sarma, A. V. S.; Vijay, D.; Sastry, N. G.; Ranganathan, S. *Chem. Eur. J.* **2007**, *13*, 4253.
- Xu, X.; Lu, Y.; Wang, E.; Ma, Y.; Bai, X. *J. Mol. Struct.* **2006**, 124.
- Min, J.; Li, J.; Chen, W.; Zhang, F.-X. *Struct. Chem.* **2006**, *17*, 327.
- Lu, J. Y.; Schauss, V. *Inorg. Chem. Commun.* **2003**, *6*, 1332.
- Wang, R.; Zhou, Y.; Sun, Y.; Yuan, D.; Han, L.; Lou, B.; Wu, B.; Hong, M. *Cryst. Growth Des.* **2005**, *5*, 251.
- Blessing, R. H. *Acta Cryst.* **1995**, *A51*, 33.
- Sheldrick, G. M. (2001). SHELXTL. Version 6. Bruker AXS Inc., Madison, Wisconsin, USA.
- Farrugia, L. J. *J. Appl. Cryst.* **1997**, *30*, 565.
- Brandenburg, K. DIAMOND. Version 2.1. Crystal Impact GbR, Bonn, Germany. 1998.
- Addison, A. W.; Rao, T. N.; Reedijk, J.; van Rijn, J.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.
- Ray, A.; Banerjee, S.; Butcher, R. J.; Desplanches, C.; Mitra, S. *Polyhedron* **2008**, *27*, 2409.
- Liu, G.-X.; Xu, Y.-Y.; Wang, Y.; Nishihara, S.; Ren, X.-M. *Inorg.*

- Chim. Acta* **2010**, 363, 3932.
28. Yin, P.-X.; Zhang, J.; Cheng, J.-K.; Li, Z.-J.; Yao, Y.-G. *Inorg. Chem. Commun.* **2006**, 9, 541.
29. Huang, W.-W.; Yang, S.-P. *Acta Cryst.* **2008**, E64, m525.
30. Koo, B. K.; Kim, J.; Lee, U. *Inorg. Chim. Acta* **2010**, 363, 1760.
31. Kim, J.; Lee, U.; Koo, B. K. *Bull. Korean Chem. Soc.* **2010**, 31, 1743.
32. Janiak, C. *J. Chem. Soc., Dalton trans.* **2000**, 3885.
33. Liu, G.-X.; Zhu, K.; Xu, H.-M.; Nishihara, S.; Huang, R.-Y.; Ren, X.-M. *CrystEngComm.* **2009**, 11, 2784.
34. Shao, M.; Li, M.-X.; Dai, H.; Lu, W.-C.; An, B.-L. *J. Mol. Struct.* **2007**, 829, 155.
35. Wang, R.-H.; Gong, Y.-Q.; Han, L.; Yuan, D.-Q.; Lou, B.-Y.; Wu, B.-L.; Hong, M.-C. *J. Mol. Struct.* **2006**, 784, 1.
36. Wang, R.; Yuan, D.; Jiang, F.; Han, L.; Gong, Y.; Hong, M. *Cryst. Growth Des.* **2006**, 6, 1351.
37. Deacon, G. B.; Phillips, R. J. *Coord. Chem. Rev.* **1980**, 33, 227.
38. Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*, 4th ed., John Wiley & Sons: New York, 1986; pp 228, 371.
39. Lazarou, K. N.; Chadjistamatis I.; Terzis, A.; Perlepes, S. P.; Raptopoulou, C. P. *Inorg. Chim. Acta* **2010**, 363, 107.
-