

Synthesis and Crystal Structures of Mn(II)- and Ni(II)-Dicarboxylate Complexes with 1,10-Phenanthroline

Bon Kweon Koo

Department of Chemistry, Catholic University of Daegu, Gyeongsbuk 712-702, Korea. E-mail: bkkoo@cu.ac.kr
Received March 2, 2012, Accepted April 13, 2012

Two new metal(II) complexes, $[\text{Mn}(\text{dpa})(\text{phen})(\text{H}_2\text{O})_2]_n$ (**1**) (H_2dpa = diphenic acid, phen = 1,10-phenanthroline) and $[\text{Ni}_2(\text{nda})(\text{phen})_2(\text{H}_2\text{O})_6](\text{nda})(\text{H}_2\text{O})$ (**2**) (H_2nda = 2,6-naphthalenedicarboxylic acid) have been synthesized and characterized by elemental analysis, infrared spectroscopy, thermogravimetric analysis, and single crystal X-ray diffraction. In complex **1**, Mn(II) ion is six-coordinated, and Mn(II) ions are bridged by dpa ligands into 1D chains. While, the complex **2** is dimer and two Ni(II) ions are bridged by one nda ligand cooperated with the terminal ligand phen. In each complex, the dicarboxylate ligand is coordinated to metal(II) ions as a bis-monodentate.

Key Words : Metal(II)-dicarboxylates, Crystal structure, Thermal properties

Introduction

Coordination polymers are of great interest due to their intriguing structural motifs and potential applications in optical, electronic, magnetic, and porous materials.¹⁻³ The most commonly used strategy for designing such materials relies on the utilization of multidentate N- or O-donor ligands which have the capacity to bridge between metal centers to form polymeric structures. Many of them are based on metal carboxylates,^{4,5} such as dicarboxylate succinate, maleate and terephthalate,⁶⁻⁹ polycarboxylate 1,3,5-benzenetricarboxylate and 1,2,4,5-benzenetetracarboxylate complexes.^{10,11} Analogous to rigid aromatic dicarboxylate terephthalate, diphenic acid and 2,6-naphthalenedicarboxylic acid are a useful source possessing several novel features besides its metrics of aromatic dicarboxylate ligands. Especially, diphenic acid 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. Up to now, many these ligand complexes were reported, such as linear complexes,^{12,13} metal-organic framework,¹⁴⁻¹⁹ and rare-earth complexes.²⁰ We present here two new dicarboxylic acid complexes $[\text{Mn}(\text{dpa})(\text{phen})(\text{H}_2\text{O})_2]_n$ (**1**) and $[\text{Ni}_2(\text{nda})(\text{phen})_2(\text{H}_2\text{O})_6](\text{nda})(\text{H}_2\text{O})$ (**2**). Complex **1** is 1D network structure in which two Mn(II) ions are bridged by dpa, while complex **2** is dinuclear compound. Both complexes are further extended into supramolecular framework by hydrogen bonds and π - π stacking interactions. Their IR spectra and thermal stability are also reported.

Experimental Section

Chemicals and Measurements. Both 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 $[\text{Mn}(\text{dpa})(\text{phen})(\text{H}_2\text{O})_2]_n$ (1**).** To a well stirred solution of diphenic acid (0.242 g, 1 mmol) in methanol (7 mL) a solution of $\text{Mn}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$ (0.245 g, 1 mmol) in methanol (3 mL) was added. The reaction mixture was stirred for 5 min, a white solid was filtered and the residue was re-dissolved in distilled water (10 mL). To this solution a solution of 1,10-phenanthroline (0.180 g, 1 mmol) in water (10 mL) was added and the solution was stirred for 30 min. The solution was allowed to evaporate slowly for several days at room temperature, which yielded yellow block crystals in good quality for X-ray crystallography. Yield: 68% (0.347 g) based on Mn. Elemental Anal. Calcd. for $\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_6\text{Mn}$: C, 61.07; H, 3.94; N, 5.48. Found: C, 61.00; H, 4.14; N, 5.48%. IR (KBr, cm^{-1}): 3565(s), 3054(m), 2954(m), 1599(s), 1577(s), 1546(s), 1531(s), 1425(s), 1401(s), 1377(s), 1144(w), 1103(w), 823(m), 812(m), 761(s), 718(m), 672(m).

Preparation of $[\text{Ni}_2(\text{nda})(\text{phen})_2(\text{H}_2\text{O})_6](\text{nda})(\text{H}_2\text{O})$ (2**).** A mixture of H_2nda (0.032 g, 0.15 mmol), phen (0.027 g, 0.15 mmol), $\text{Ni}(\text{OAc})_2\cdot 4\text{H}_2\text{O}$ (0.037 g, 0.15 mmol), NaOH aqueous solution (0.1 mL, 0.65 mol/L), 8 mL distilled H_2O and 2 mL ethanol was placed in a 23 mL Teflon-lined stainless steel autoclave, and the vessel was sealed and heated to 100 $^\circ\text{C}$ for 4 days, then cooled to room temperature. The resulting blue block crystals were filtered off and washed with ethanol and then dried at room temperature. Yield: 78% (0.06 g) based on Ni. Elemental Anal. Calcd. for $\text{C}_{48}\text{H}_{42}\text{N}_4\text{O}_{15}\text{Ni}_2$: C, 55.85; H, 4.10; N, 5.43. Found: C, 55.98; H, 4.21; N, 5.37%. IR (KBr, cm^{-1}): 3595(w), 3065(s), 1602(m), 1543(vs), 1493(m), 1395(vs), 1357(s), 845(w), 792(w), 724(w).

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

Complex	1	2
Empirical formula	C ₂₆ H ₂₀ N ₂ O ₆ Mn	C ₄₈ H ₄₂ N ₄ O ₁₅ Ni ₂
Formula weight	511.38	1032.26
T (K)	200(2)	200(2)
λ (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2(1)/ <i>n</i>	<i>P</i> -1
<i>a</i> (Å)	10.5871(9)	10.3519(12)
<i>b</i> (Å)	10.8513(10)	10.7178(13)
<i>c</i> (Å)	19.7147(18)	11.2318(13)
α (°)		73.944(3)
β (°)	90.199(2)	87.503(2)
γ (°)		70.679(2)
<i>V</i> (Å ³)	2264.9(4)	1128.5(2)
<i>Z</i>	4	1
μ (mm ⁻¹)	0.630	0.911
<i>F</i> (000)	1052	532
θ (°)	2.07 to 28.27	1.89 to 28.31
Absorption correction	none	none
Limiting indices	-14 ≤ <i>h</i> ≤ 11, -14 ≤ <i>k</i> ≤ 13, -26 ≤ <i>l</i> ≤ 26	-13 ≤ <i>h</i> ≤ 13, -8 ≤ <i>k</i> ≤ 14, -11 ≤ <i>l</i> ≤ 14
Reflections collected	16453	8424
Independent reflections	5592 [R(int) = 0.0748]	5509 [R(int) = 0.0261]
Observed reflections [<i>I</i> ≥ 2σ(<i>I</i>)]	2785	3956
Goodness-of-fit on <i>F</i> ²	0.921	1.157
<i>R</i> ₁ [<i>I</i> ≥ 2σ(<i>I</i>)]	0.0512	0.0853
<i>wR</i> ₂ [<i>I</i> ≥ 2σ(<i>I</i>)]	0.1044	0.2099
<i>R</i> ₁	0.1239	0.1305
<i>wR</i> ₂	0.1423	0.2865
Largest peak and hole (eÅ ⁻³)	0.551 and -0.723	1.433 and -2.101

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 ($\theta = 0.71073$ Å) at the Korea Basic Science Institute. The structures were solved by direct method and refined on *F*² by full-matrix least-squares procedures using the SHELXTL programs.²¹ All non-hydrogen atoms were refined using anisotropic thermal parameters. The 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 ORTEP-3²² or DIAMOND program.²³ The crystallographic data for complexes **1** and **2** are listed in Table 1.

Results and Discussion

Description of the Structures. The asymmetric unit of complex **1** consists of one Mn(II) ion, one dpa ligand, one chelating phen ligand and two coordinated water molecules

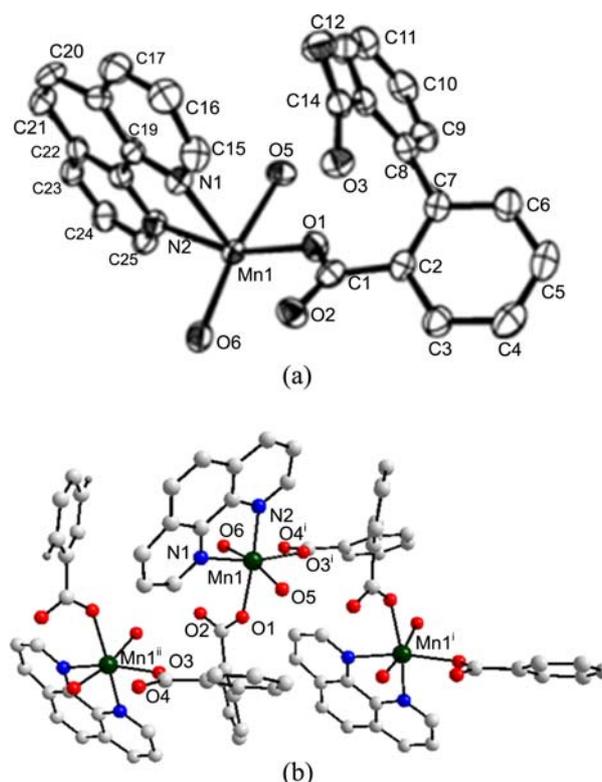
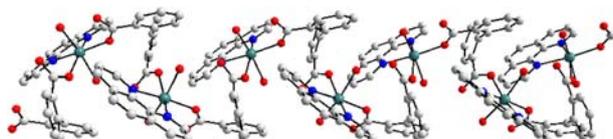


Figure 1. (a) Asymmetric unit and (b) molecular structure of complex **1** with atomic labeling [symmetry codes: i) 3/2-*x*, -1/2+*y*, 1/2-*z*; ii) 3/2-*x*, 1/2+*y*, 1/2-*z*]. All H atoms are omitted for clarity.

(Fig. 1(a)). In the molecular structure (Fig. 1(b)), each Mn(II) ion center is six-coordinated by two nitrogen atoms (N1, N2) from one phen ligand, two oxygen atoms of the carboxylate (O1, O3ⁱ) from two dpa ligands and two oxygen atoms of water molecules. The Mn-N bond lengths are slightly longer than the Mn-O distances. The basal plane (N1, N2, O1, O3ⁱ) is nearly planar (mean deviation 0.098(3) Å) and the Mn1 is displaced by 0.176(1) from the plane toward O6. The structural data (Table 2) are in agreement with those of the metal(II) complexes (metal = Mn, Co, Ni) which exhibit the similar geometry.²⁴⁻³⁰ The dpa ligand adopts bis-monodentate coordination mode. Mn(II) ions (Mn1...Mn1ⁱ = 6.583(1) Å) are bridged by dpa ligands into 1D chains along *b*-axis (Fig. 2). Two planes [C2-C7 and C8-C13] in dpa are nearly planar with mean deviation of 0.013(4) and 0.005(4) Å, respectively, the dihedral angle between them being 70.6(1)°. The phen molecules are also nearly planar [the largest deviation of atoms from the mean plane is C16 atom, -0.111(4) Å]. The phen ligands locate at both sides of the chain. The 1D chain is further extended by the C-H...O hydrogen bonds into a 2D network (Fig. 3). The intrachain hydrogen bonds (C15-H15...O3, C16-H16...O4) between the phen ligands and the oxygen atoms of the carboxylates (coordinated and uncoordinated) contribute to the stabilization of the chain structures. The interchain hydrogen bonds (C23-H23...O4) between the phen ligands and the uncoordinated oxygen atoms of the carboxylates link the chains into 2D networks along the *a*-axis. The distance

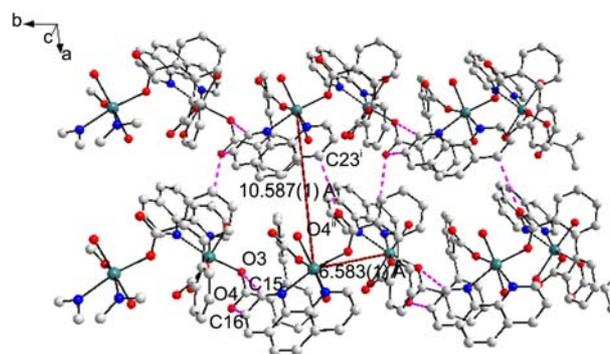
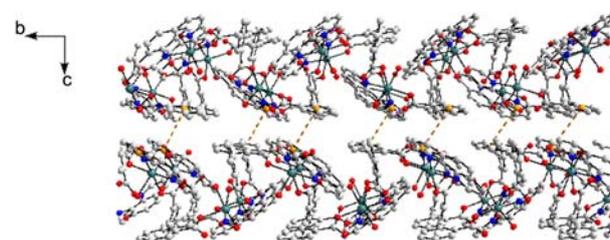
Table 2. Selected bond lengths (Å) and angles (°) for complex 1 and 2

Complex 1			
Mn1–O3 ⁱ	2.143(2)	Mn1–O1	2.153(2)
Mn1–O6	2.218(2)	Mn1–O5	2.229(2)
Mn1–N2	2.262(3)	Mn1–N1	2.288(3)
O1–C1	1.256(4)	O2–C1	1.268(4)
O3–C14	1.263(4)	O4–C14	1.256(4)
O3i–Mn1–O1	102.54(9)	O3i–Mn1–O6	90.47(9)
O1–Mn1–O6	89.94(9)	O3i–Mn1–O5	92.01(9)
O1–Mn1–O5	78.54(9)	O6–Mn1–O5	168.49(9)
O3i–Mn1–N2	91.87(10)	O1–Mn1–N2	159.45(10)
O6–Mn1–N2	104.68(10)	O5–Mn1–N2	86.48(10)
O3i–Mn1–N1	165.08(10)	O1–Mn1–N1	91.16(10)
O6–Mn1–N1	95.49(10)	O5–Mn1–N1	84.86(10)
N2–Mn1–N1	73.40(10)		
Symmetry transformations used to generate equivalent atoms: i) 3/2–x, –1/2+y, 1/2–z			
Complex 2			
Ni1–O1	2.051(4)	Ni1–O7	2.060(4)
Ni1–O5	2.085(5)	Ni1–N2	2.093(6)
Ni1–O6	2.093(5)	Ni1–N1	2.095(5)
O1–C13	1.229(8)	O2–C13	1.233(9)
O3–C19	1.263(8)	O4–C19	1.251(8)
O1–Ni1–O7	86.69(17)	O1–Ni1–O5	90.3(2)
O7–Ni1–O5	172.92(19)	O1–Ni1–N2	91.1(2)
O7–Ni1–N2	93.3(2)	O5–Ni1–N2	93.1(2)
O1–Ni1–O6	97.7(2)	O7–Ni1–O6	85.44(18)
O5–Ni1–O6	88.6(2)	N2–Ni1–O6	171.0(2)
O1–Ni1–N1	170.6(2)	O7–Ni1–N1	94.70(19)
O5–Ni1–N1	89.3(2)	N2–Ni1–N1	79.5(2)
O6–Ni1–N1	91.68(19)		


Figure 2. The 1D chain of complex 1. All H atoms are omitted for clarity.

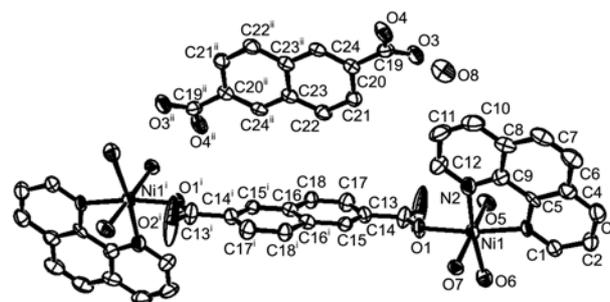
of Mn...Mn between the Mn(II) ions of adjacent chains is 10.587(1) Å. The details of hydrogen bonds are listed in Table 3. Besides, there are π - π stacking interactions between phen molecules and dpa ligands with face-to-face distance of 4.636(1) Å along *c*-axis (Fig. 4), which brings the formation of a 3D network.

In contrast to the complex 1, the structure of 2 consists of dinuclear species [Ni₂(nda)(phen)₂(H₂O)₆], one nda²⁻ counter ion, and one lattice water (Fig. 5). In the dinuclear unit, each nickel(II) ion exhibits a slightly distorted octahedral environments with the *cis*- and *trans*- L-Ni-L angles in the range of 79.5(2)–97.7(2)° and 170.6(2)–172.9(2)°, respectively (Table 2), comparable to those of the complex 1 (*cis*-L-Mn-L = 73.40–104.68, *trans*-L-Mn-L = 159.45–168.49°). Two oxygen atoms, one (O1) from nda ligand, the other (O6) from one


Figure 3. 2D-network formed by interchain C-H...O hydrogen bond in complex 1 [symmetry codes: i) –1+x, y, z; ii) 3/2–x, –1/2+y, 1/2–z]. All H atoms are omitted for clarity.

Figure 4. Packing diagram of complex 1. showing the π - π stacking. All H atoms are omitted for clarity.

water molecule, and two nitrogen atoms (N1, N2) from phen ligand constitute the equatorial plane. Two oxygen atoms (O5, O7) from water molecules occupy the axial positions. The basal plane (N1N2O1O6) is nearly planar (mean deviation 0.024(5) Å) and the Ni1 is displaced by 0.010(1) from the plane toward O5. The Ni-N distance is slightly longer than that of Ni-O as expected in complex 1. The distance of Ni-N and Ni-O is slightly shorter than the distances of Mn-N and Mn-O in complex 1, respectively. The structural data (Table 2) are in agreement with those of the Ni(II) complexes which exhibit the similar geometry.^{31–33}

There are two kinds of crystallographically independent nda ligands in complex 2. One is coordinated to Ni(II) ions and the other is free. The coordinated nda ligand adopts bimonodentate mode and bridges two Ni(II) ions (Ni1...Ni1ⁱ = 13.154(2) Å). The terminal phen ligands locate at both sides of the dimer. The planes of nda and phen ligands in the


Figure 5. The molecular structure of complex 2 with the atomic labeling [symmetry codes: i) 2–x, –y, 2–z; ii) 1–x, –y, 2–z]. All H atoms are omitted for clarity.

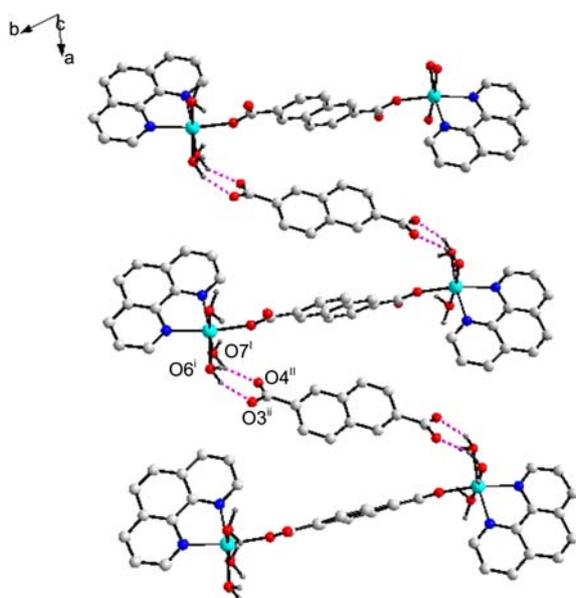


Figure 6. The 1D chain structure (along *a*-axis) by O–H⋯O hydrogen bond in complex **2** [symmetry codes: i) *x*, *1+y*, *-1+z*; ii) *1+x*, *1+y*, *-1+z*]. All C–H hydrogen atoms are omitted for clarity.

complex are nearly planar with mean deviation of 0.006(7) (coordinated) and 0.000(0) (free), and 0.025(7) Å, respectively. The dihedral angles between *nda* ligand (coordinated) and *phen* ligand are 72.5(1)°. And, the dihedral angles between *nda* ligands (coordinated and uncoordinated) is 71.9(1)°. The dimers are interlinked by hydrogen bonds (C–H⋯O, O–H⋯O) and π - π stacking interactions to form supramolecular 3D network. The hydrogen bonds (O6–H6⋯O3, O7–H7⋯O4) between the free *nda* ligand and the coordinated water molecules form 1D chains along *a*-axis (Fig. 6). The chains are interlinked by hydrogen bonds (C15–H15⋯O7, C18–H18⋯O7) between coordinated *nda* ligand of adjacent chain and coordinated water, and π - π stacking interactions between *phen* molecules and the free *nda* ligands with face-to-face distance of 3.749(1) Å to form 2D network along *b*-axis (Fig. 7). In addition, O–H⋯O hydrogen bonds between the lattice water molecules and free *nda* ligands (O⋯O distance: 2.681 Å) or coordinated water molecules (O⋯O distance: 2.895 Å), and between lattice water molecules (O⋯O distance: 2.626 Å) contribute

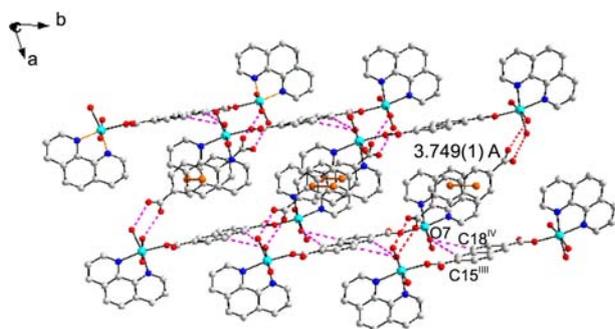


Figure 7. 2D network of complex **2**, showing the hydrogen bonds and π - π interactions. All H atoms are omitted for clarity.

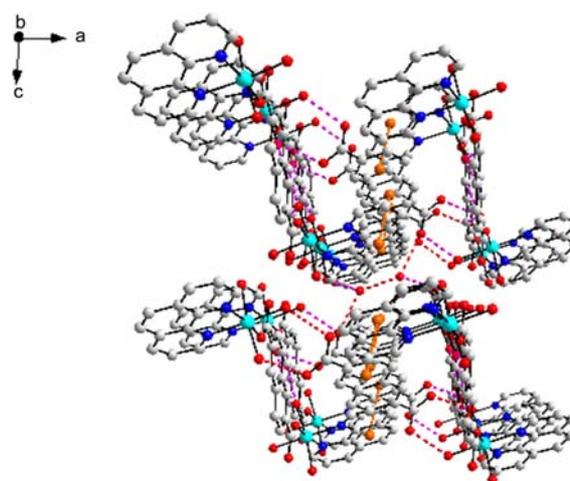


Figure 8. Packing diagram of complex **2** viewed along *b*-axis. All H atoms are omitted for clarity.

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

Donor–H...acceptor	D–H	H...A	D...A	D–H...A
Complex 1				
C15–H15...O3	0.95	2.66	3.50(1)	147.8
C16–H16...O4	0.95	2.82	3.50(1)	129.2
C23 ⁱ –H23...O4 ⁱⁱ	0.95	2.87	3.67(1)	143.3
Symmetry codes: i) $-1+x, y, z$; ii) $3/2-x, -1/2+y, 1/2-z$.				
Complex 2				
O6 ⁱ –H6B...O3 ⁱⁱ	0.98	1.82	2.67(1)	142.3
O7 ⁱ –H7A...O4 ⁱⁱ	0.98	1.82	2.72(1)	150.8
C15 ⁱⁱⁱ –H15...O7	0.95	2.70	3.50(1)	141.4
C18 ^{iv} –H18...O7	0.95	2.72	3.50(1)	141.0
Symmetry codes: i) $x, 1+y, -1+z$; ii) $1+x, 1+y, -1+z$; iii) $x, 1+y, z$; iv) $2-x, 1-y, 2-z$.				

significantly to the assembly of these dimeric units into supramolecular 3D network (Fig. 8). The details of hydrogen bonds 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 between 1357 and 1602 cm^{-1} in the IR spectra of two complexes can be assigned to symmetric stretching vibration $\nu_s(\text{COO}^-)$ and asymmetric stretching vibration $\nu_{as}(\text{COO}^-)$ of the coordinated carboxylates groups.³⁴ The absence of such bands at around 1700 cm^{-1} indicates the complete deprotonation of H₂dpa and H₂nda. All this agrees well with the result of X-ray single crystal analysis. The IR spectra also show the bands at 3054–3595 cm^{-1} corresponding to the vibration absorption of coordinated water and lattice water, respectively.^{35,36}

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. 9). The TG curves are divided into four stages (Fig. 9). For complex **1**, the first weight loss of 7.57% between 117 and 184 °C with an endothermic peak at 171 °C

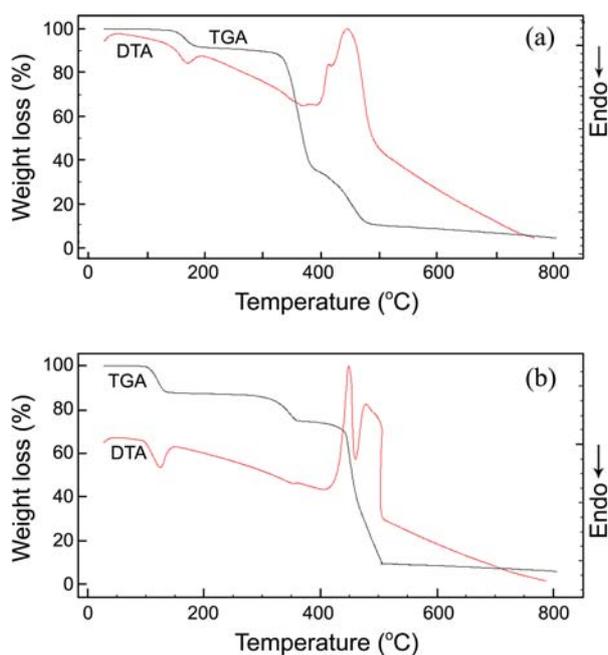


Figure 9. TGA curves of (a) complex **1** and (b) complex **2**.

corresponds to the loss of two coordinated water molecules per formula unit (calc. 7.05%). Upon further heating up to 495 °C, the anhydrous compositions show two indistinct weight loss stages with 82.19% in total (calc. 82.21%) corresponding to the decomposition of organic ligands. The remaining product collapses slowly beyond this temperature to the 800 °C. The complex **2** shows the first weight loss of 12.03% (calc. 12.22%) from 96 to 139 °C with an endothermic peak at 125 °C, which corresponds to the release of coordinated water and lattice water molecules. Over 139–505 °C, the sample loses the additional weight of 78.54% (calc. 76.41%) corresponding to the decomposition of organic ligands in two steps overlapping to each other. These weight losses are accompanied by two exothermic effect on the DTA curve with maximum at 448 and 478 °C, respectively.

Conclusion

Two novel metal(II) complexes, $[\text{Mn}(\text{dpa})(\text{phen})(\text{H}_2\text{O})_2]_n$ (**1**) and $[\text{Ni}_2(\text{nda})(\text{phen})_2(\text{H}_2\text{O})_6](\text{nda})(\text{H}_2\text{O})$ (**2**) were prepared using dicarboxylates as bridging ligand. In each complex, the dicarboxylate ligand is coordinated to metal ions as a bis-monodentate. The manganese complex of **1** exhibits 1D network structure. While, the complex **2** is dinuclear nickel(II) complex bridged by nda ligand. 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 and conventional 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 868922 for **1** and 868923 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 2012 Research Fund of Catholic University of Daegu. The author also acknowledges the Korea Basic Science Institute for providing the crystal structure results.

References

- Yaghi, O. M.; O'Keeffe, M.; Ockwig, N. W.; Chae, H. K.; Eddaoudi, M.; Kim, J. *Nature* **2003**, *423*, 705.
- Hagman, P. J.; Hagman, D.; Zubieta, J. *Angew. Chem. Int. Ed.* **1999**, *38*, 2638.
- Erxleben, A. *Coord. Chem. Rev.* **2003**, *246*, 203.
- Rao, C. N. R.; Natarajan, S.; Vaidhyanathan, R. *Angew. Chem. Int. Ed.* **2004**, *43*, 1466.
- Kim, J.; Lee, U.; Koo, B. K. *Bull. Korean Chem. Soc.* **2010**, *31*, 487.
- Kim, J.; Lee, U.; Koo, B. K. *Bull. Korean Chem. Soc.* **2010**, *31*, 1743.
- Koo, B. K.; Kim, J.; Lee, U. *Inorg. Chim. Acta* **2010**, *363*, 1760.
- Go, Y. B.; Wang, X.; Anokhina, E. V.; Jacobson, A. J. *Inorg. Chem.* **2005**, *44*, 8265.
- Xu, H.; Wang, R.; Li, Y. *J. Mol. Struct.* **2004**, *688*, 1.
- Yaghi, O. M.; Li, H.; Davis, C.; Richardson, D.; Groy, T. L. *Acc. Chem. Res.* **1998**, *31*, 474.
- Hao, N.; Li, Y. G.; Wang, E. B.; Shen, E. H.; Hu, C. W.; Xu, L. *J. Mol. Struct.* **2004**, *697*, 1.
- Shi, Q.; Sun, Y.; Sheng, L.; Ma, K.; Cai, X.; Liu, D. *Inorg. Chim. Acta* **2009**, *362*, 4167.
- Wang, R.; Zhou, Y.; Sun, Y.; Yuan, D.; Han, L.; Lou, B.; Wu, B.; Hong, M. *Crystal Growth & Design* **2005**, *5*, 251.
- Guo, F.; Xu, J.; Zhang, X.; Zhu, B. *Inorg. Chim. Acta* **2010**, *363*, 3790.
- Yin, P.-X.; Zhang, J.; Li, Z.-J.; Qin, Y.-Y.; Cheng, J.-K.; Yao, Y.-G. *Inorg. Chem. Commun.* **2008**, *11*, 134.
- Su, Z.; Fan, J.; Chen, M.; Okamura, T.-A.; Sun, W.-Y. *Crystal Growth & Design* **2011**, *11*, 1159.
- Huang, W.-W.; Yang, S.-P. *Acta Cryst.* **2008**, *E64*, m525.
- Rosi, N. L.; Kim, J.; Eddaoudi, M.; Chen, B.; O'Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005**, *127*, 1505.
- Volkringer, C.; Marrot, J.; Férey, G.; Loiseau, T. *Crystal Growth & Design* **2008**, *8*, 685.
- Liu, Q.-Y.; Wang, W.-F.; Wang, Y.-L.; Shan, Z.-M.; Wang, M.-S.; Tang, J. *Inorg. Chem.* **2012**, *51*, 2381.
- Sheldrick, G. M., SHELXTL. Version 6. Bruker AXS Inc., Madison, Wisconsin, USA, 2001.
- Farrugia, L. J. *J. Appl. Cryst.* **1997**, *30*, 565.
- Brandenburg, K. DIAMOND. Version 2.1. Crystal Impact GbR, Bonn, Germany. 1998.
- Shao, M.; Li, M.-X.; Dai, H.; Lu, W.-C.; An, B.-L. *J. Mol. Struct.* **2007**, *829*, 155.
- Singh, W. M.; Baruah, J. B. *Inorg. Chim. Acta* **2009**, *362*, 4268.
- Zhou, J.; Sun, C.; Jin, L. *J. Mol. Struct.* **2007**, *832*, 55.
- Zheng, Y.-Q.; Lin, J.-L.; Kong, Z.-P. *Inorg. Chem.* **2004**, *43*, 2590.
- An, Z.; Niu, X.-C. *Acta Cryst.* **2008**, *E64*, m1547.
- Tian, D.; Pang, Y.; Guo, S.; Zhu, X.; Zhang, H. *J. Coord. Chem.*

- 2011**, *64*, 1006.
30. Du, L.; Fang, R.-B.; Zhao, Q.-H. *Acta Cryst.* **2007**, *E63*, m1439.
31. Li, J.-H.; Nie, J.-J.; Xu, D.-J. *Acta Cryst.* **2008**, *E64*, m1108.
32. Kongshaug, K. O.; Fjellvåg, H. *Solid State Sciences* **2003**, *5*, 303.
33. Lee, S. W.; Kim, H. J.; Lee, Y. K.; Park, K.; Son, J.-H.; Kwon, Y.-U. *Inorg. Chim. Acta* **2003**, *353*, 151.
34. Liu, G.-X.; Zhu, K.; Xu, H.-M.; Nishihara, S.; Huang, T.-Y.; Ren, X.-M. *CrystEngComm.* **2009**, *11*, 2784.
35. Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*, 4th ed.; John Wiley & Sons: New York, 1986; p 228, 371.
36. Lazarou, K. N.; Chadjistamatis I.; Terzis, A.; Perlepes, S. P.; Raptopoulou, C. P. *Inorg. Chim. Acta* **2010**, *363*, 107.
-