Electronic Supplementary Material (ESI) for CrystEngComm

Supporting Information for

Structure Evolution and Coordination Modes of Metal-Carboxylate Frameworks with Robust Linear Trinuclear Complexes as Building Units

YooJin Kim[a,b] and Duk-Young Jung[a]*

[a]*Department of Chemistry-BK21 and Institute of Basic Sciences, Sungkyunkwan Advanced Institute of Nanotechnology, Sungkyunkwan University, Suwon 440-746, Korea* .

[b]*Engineering Ceramic Center, Korea Institute of Ceramic Engineering and Technology, Icheon 467-843, Korea*.

Fax: +82-31-290-7075; Tel: +82-31-290-7074; E-mail: dyjung@skku.edu

*Author to whom correspondence should be addressed; E-mail: dyjung@skku.edu

Experimental Section

Synthetic Procedures. $Mn_3(obc)_3(bpy)_2$ (1).

$Mn_3(obc)_3(bpy)_2$ (1).

Method A. A sample of **1** was prepared easily by the ligand substitution reaction of $Mn_3(CO_2CH_3)_6(bpy)_2$ [1] complex in ethanol with an excess of $obcH_2$ ligand. The $MeCO_2H$ was substituted by $obcH_2$ as the hydrothermal method and large crystal was obtained. Solvo-thermal reaction of $Mn_3(CO_2CH_3)_6(bpy)_2$ (0.1g, 0.01mol) and $obcH_2$ (0.2g, 0.03mol) in ratio of 1:3 at 180°C for 1day afforded a large amount of yellow crystals of **1.** The solid phase was collected by filtration, washed with distilled water and dried at room temperature.

Method B. A mixture of 0.3 g (1 mmol) of $Mn(NO_3)_2 \cdot 6H_2O$, 0.26 g (1 mmol) of obc and 0.16 g (1mmol) of bpy with $Mn(NO_3)_2$: obc : bpy molar ratios of 1:1.0:1.0 were heated along with 3 ml of water and 5 ml ethanol in a 23 ml capacity Teflon-lined reaction vessel at 180°C for 1 day and then cooled to room temperature by quenching in cold water bath. Dark yellow large crystal obtained. The structure was determined by X-ray crystallography. The X-ray powder diffraction for the prepared samples gave us the same patterns with the

simulated XRPD data according to the single crystal X-ray diffraction data (Fig. S5). FT-IR (KBr, cm^{-1}) 1697, 1595, 1536, 1503, 1412, 1388, 1324, 1294, 1248 (Fig. S6).

$[Co_3(obc)_3(bpy)_2](H_2O)$ (2) and **$[Ni_3(obc)_3(bpy)_2](H_2O)$ (3)**.

Compounds of **2** and **3** were synthesized similar method of compound **1** except that $Mn(NO_3)_2 \cdot 6H_2O$ was used instead of $Co(NO_3)_2 \cdot 6H_2O$ for **2** and $Ni(NO_3)_2 \cdot 6H_2O$ for **3**, respectively. In particle, large violet and pale green crystal for **2** and **3**, respectively were obtained though the method B.

$[Mn_3(obc)_3(phen)_2](2H_2O)$ (4), $Co_3(obc)_3(phen)_2$ (5)

Compound **4** and **5** were synthesized similar method of compound **1** and **2** except for 1,10-phenonthroline (0.18g, 1mmol) was used in place of 2,2-bipyridine. Compound **4** and **5** were used $M(NO_3)_2 \cdot 6H_2O$,(M = Mn and Co).

X-ray Crystallographic studies

Single-crystal X-ray data of **1**, **2** and **3** were collected on a Siemens P4 automated four-circle diffractometer equipped with graphite monochromated Mo Kα radiation (λ = 0.71079 Å). Crystal and intensity data of **4** and **5** were collected at 173 K using a SMART CCD diffractometer with graphite-monochromated Mo Kα radiation (0.71073 Å). Cell

parameters were determined and refined by the SMART program.[2] Data reduction was performed using SAINT software, which corrects for Lorentz and polarization effects.[3] Empirical absorption correction was applied with the SADABS program.[4] The structure of **1, 2** and **3** are solved by patterson methods (using the PATT options) and the standard difference Fourier techniques (SHELX-97)[5]. The structure of **4** and **5** are solved by direct methods (using the TREF options) All non-hydrogen atoms were refined anisotropically except water molecules. All hydrogen atoms on benzene rings were calculated at idealized positions (HFIX 43). Hydrogen atoms for **2, 3** and **4** could not be found in the crystal structure refinements because of their low electron densities

Single crystals with dimensions 0.5 × 0.2 × 0.1 mm^3 (**1**) 0.32 × 0.30 × 0.28 mm^3 (**2**) 0.28 × 0.24 × 0.16 mm^3 (**3**) 0.40 × 0.15 × 0.15 mm^3 (**4**) 0.25 × 0.15 × 0.13 mm^3 (**5**) were selected for the crystal structure analyses. The unit-cell parameters for **1 - 5** suggested a monoclinic unit cell with two possible space groups *C*2/*c* and *C*2. A statistical analysis of reflection intensities suggested centro-symmetric the space group, and the structure analysis converged on in *C*2/*c* (no. 15). The summary of crystal data for **1 - 5** is represented in Table S1 and Table S2.

Anal. Calcd, for **1** (%) : C 59.72, H 3.24 N 4.50; Found: C 59.32, H 3.13 N 4.53. Anal.

Calcd, for **2** (%) : C 58.32, H 3.32 N 4.39; Found: C 58.40, H 3.22 N 4.25. Anal. Calcd, for **3** (%) : C 58.35, H 3.33 N 4.39; Found: C 57.90, H 3.12 N 4.55. Anal. Calcd, for **4** (%) : C 58.85, H 3.30 N 4.16; Found: C 60.45, H 3.45 N 4.24. Anal. Calcd, for **5** (%) : C 60.65, H 3.09 N 4.29; Found: C 60.02, H 3.02 N 4.32.

CCDC *795499-795503* can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif

Table S1 Crystal and structure refinement details of **1**, **2** and **3**

compound	**1**	**2**	**3**
formula	$C_{62}H_{40}Mn_3O_{15}N_4$	$C_{62}H_{42}Co_3O_{16}N_4$	$C_{62}H_{42}Ni_3O_{16}N_4$
fw	1245.80	1275.79	1275.07
crystal system	monoclinic	monoclinic	monoclinic
space group	*C*2/*c* (No. 15)	*C*2/*c* (No.15)	*C*2/*c* (No. 15)
T (K)	296(2)	297(2)	296(2)
a (Å)	14.271(4)	15.213(3)	15.163(5)
b (Å)	17.077(4)	16.590(2)	16.373(4)
c (Å)	25.897(6)	23.677(3)	23.383(5)
α (deg)	90	90	90
β (deg)	92.986(11)	97.497(16)	97.486(18)
γ (deg)	90	90	90
V (Å^3)	6303(3)	5924.7(16)	5756(3)
Z	4	4	4
D_{calcd} (mg cm^{-3})	1.313	1.428	1.469
μ(Mo K),mm^{-1}	0.658	0.902	1.046
goodness-of-fit on F^2	1.119	1.024	1.033

final R_1 [a]	0.0467	0.0697	0.0740
final wR_2 [b]	0.1140	0.1810	0.1867

Table S2. Crystal and structure refinement details of **4** and **5**

compound	**4**	**5**
formula	$C_{66}H_{44}Mn_3O_{17}N_4$	$C_{66}H_{40}Co_3O_{15}N_4$
fw	1345.88	1305.81
crystal system	monoclinic	monoclinic
space group	*C*2/*c* (No. 15)	*C*2/*c* (No.15)
T (K)	296(2)	253(2)
a (Å)	15.2012(11)	15.138(2)
b (Å)	16.7136(12)	16.501(2)
c (Å)	25.8544(19)	25.844(4)
α (deg)	90	90
β (deg)	90.260(1)	91.021(2)
γ (deg)	90	90
V (Å^3)	6568.7(8)	6454.8(15)
Z	4	4
D_{calcd} (mg cm^{-3})	1.389	1.344
μ(Mo K),mm^{-1}	0.641	0.829
goodness-of-fit on F^2	1.071	0.987
final $R_1{}^a$	0.0451	0.0599
final $wR_2{}^b$	0.1111	0.1354

References

1. S. Menage, S. E. Vitols, P. Bergerat, E. Codjovi, O. Kahn, J. J. Girerd, M. Guillot, X. Solans and T. Calvet, *Inorg. Chem*., 1991, **30**, 2666.

2. SMART, version 5.0; data collection software; Bruker AXS, Inc.: Madison, WI, 1998.

3. SAINT, version 5.0; data integration software; Bruker AXS, Inc.: Madison, WI, 1998.

4. G. M. Sheldrick, SADABS, A program for absorption correction with the Bruker SMART system; Universitat Göttingen: Göttingen, Germany, 1996.

5. P. McArdle, SHELX-86 and SHELX-97 Users Guide: Crystallography Center, Chemistry Department, National University of Ireland: Galway, Ireland; *J. Appl. Crystallogr.*, 1995, **28**, 65.

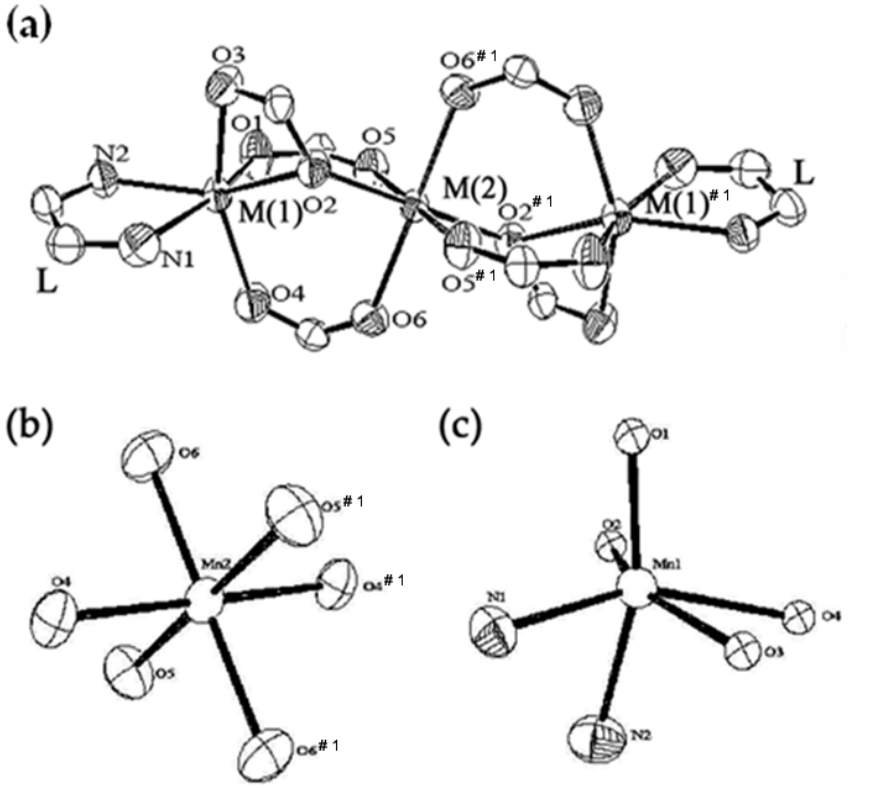

Fig. S1 (a) Schematic structure of $M_3(O_2CR)_6(L)_2$ unit for **1, 4** and **5.** Coordination environment of (b) $M(2)O_6$ and (c) $M(1)N_2O_4$. #1 -x-1/2,-y+1/2,-z+1

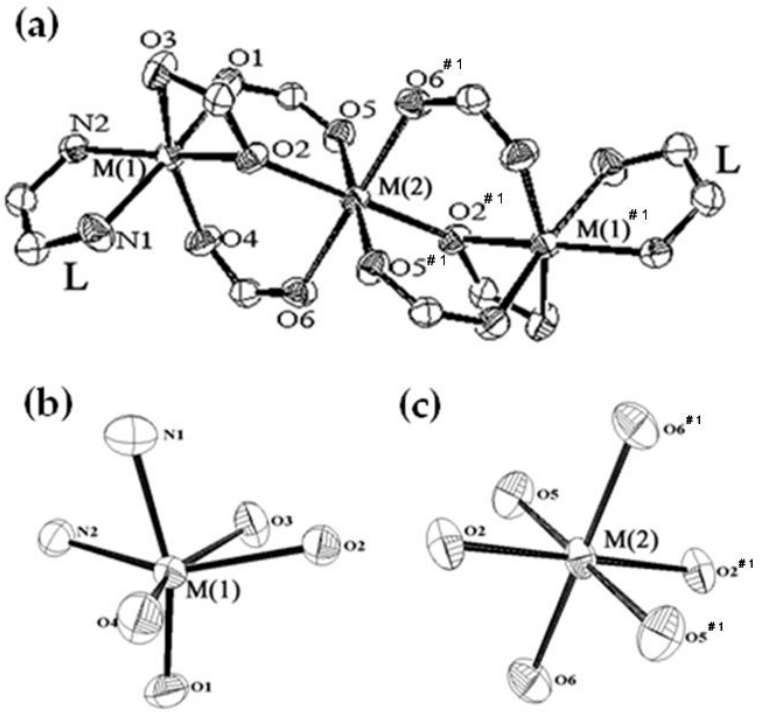

Fig. S2 (a) Schematic structure of $M_3(O_2CR)_6(L)_2$ unit for **2** and **3.** (b) Coordination environment of $M(1)N_2O_4$ and (c) $M(2)O_6$. #1 -x-1/2,-y+1/2,-z+1

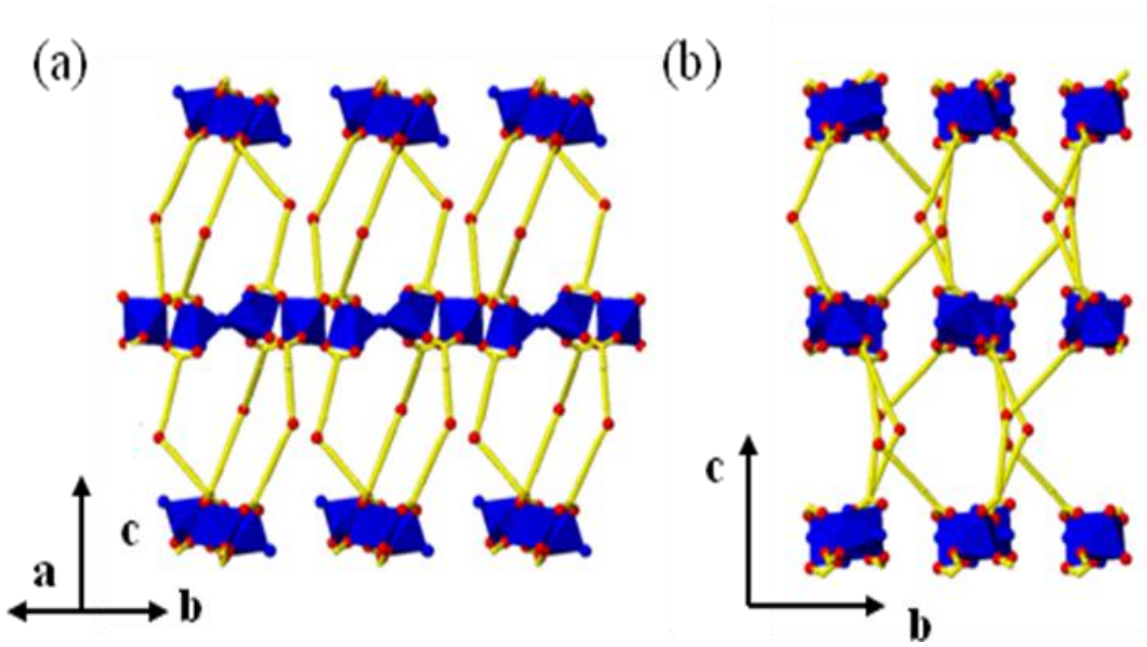

Fig. S3. The crystal structure of compounds **1, 4** and **5** (a) along [110] (b) along [100].

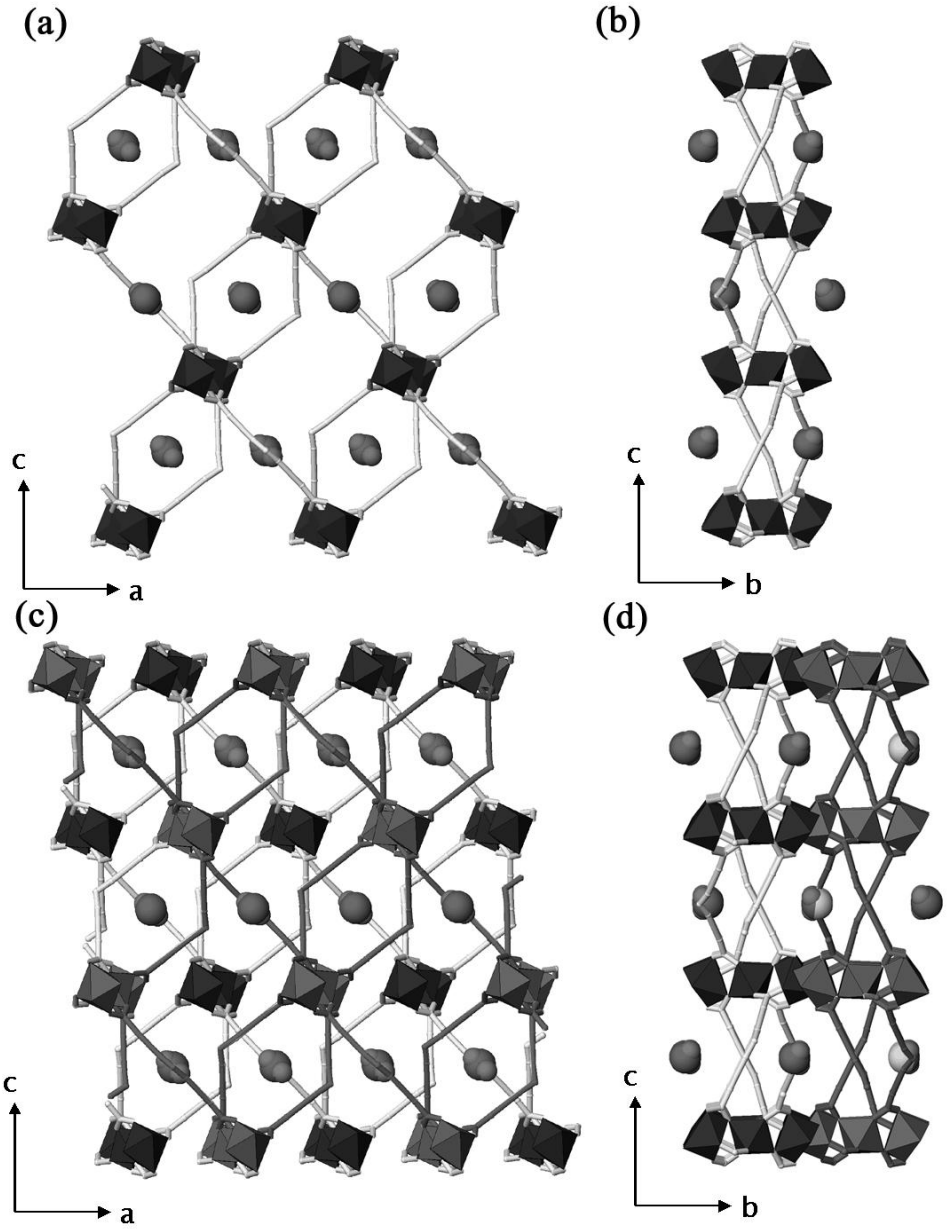

Fig. S4. (a) Crystal structure of **2** and **3** along [010] (b) along [100] in one layer. (c) Crystal structure of **2** and **3** along [010] (d) along [100] in two layers. Water molecules represented by their space-filling mode.

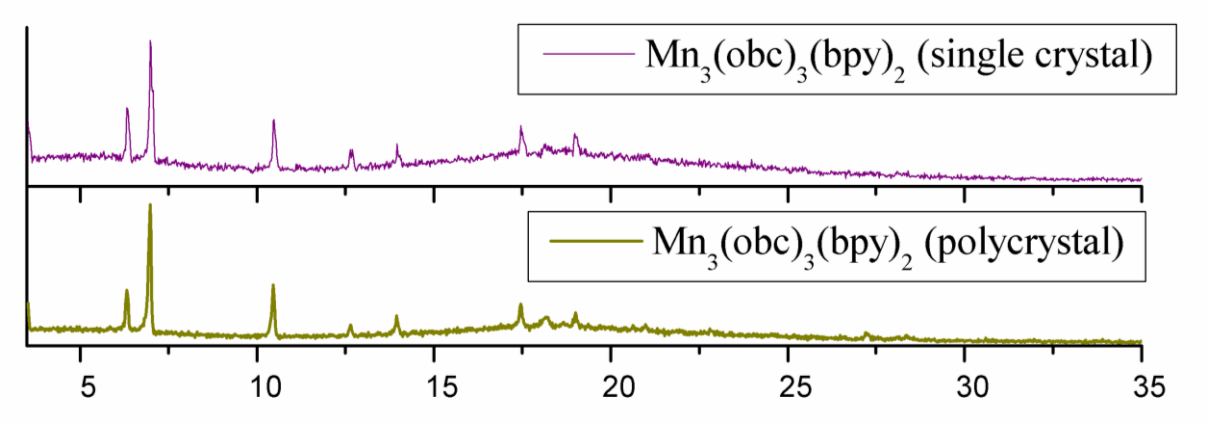

Fig. S5. XRPD spectra for single crystal and polycrystalline samples of **1**.

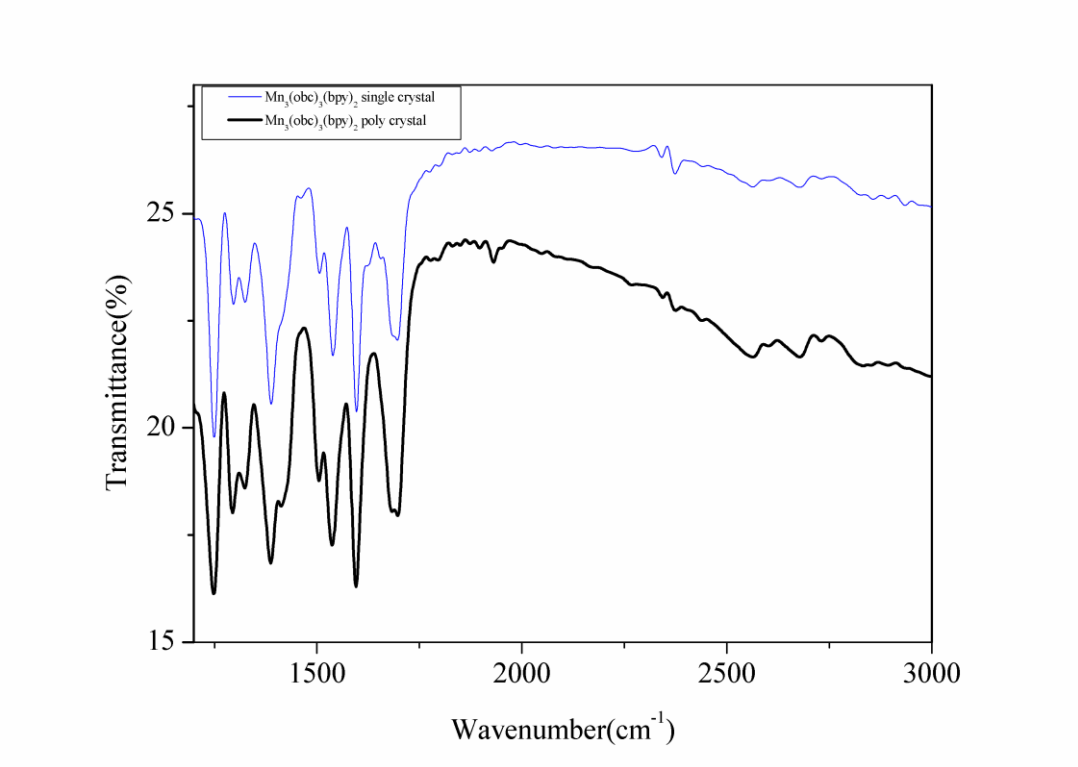

Fig. S6 FT-IR spectra for single crystal and poly crystal samples of **1**.