

용매의 분해로부터 형성된 3-차원 유기-금속 구조체, [Zn(HCOO)₃](C₂H₈N)의 합성에 미치는 영향들

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Factors in the Synthesis of 3-D Metal-Organic Framework, [Zn(HCOO)₃](C₂H₈N), Derived from Decomposition of Solvent

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INTRODUCTION

Metal-organic frameworks (MOF) have attracted much more attention recently not only for their potential applications in gas storage, separation, magnetism, nonlinear optics, luminescence, and catalysis but also for their rational design principles to construct intriguing architectures and topologies.^{1,2} In particular, benzenedicarboxylic acids have been studied extensively as ideal ligands for designing coordination polymers and open framework structures.³ In contrast, only a few coordination polymers based on flexible ligands have been reported so far probably due to their low symmetry and the flexibility of the backbones which make it more difficult to control the final coordination networks.⁴ Cyclohexanedicarboxylic acids was also expected to be useful ligands in the preparation of MOF because of their excellent bridging ability and limited flexibility. Therefore, MOFs constructed from

cyclohexane-dicarboxylic acids have attracted attention very recently.⁵

Many factors play important role in the synthesis of MOFs such as the coordination geometry of metal ions,⁶ structures of organic ligands,⁷ the solvent system employed,⁸ counteranions,⁹ and molar ratios of ligands to metal ions.¹⁰ Hydrothermal or solvothermal reactions are mostly employed in the preparation of MOFs, and some unexpected and interesting MOFs have been obtained in these processes.¹¹ In the synthesis of [Zn(BDC)(DMF)] (BDC = benzene-1,4-dicarboxylic acid and DMF = dimethyl formamide), an additional phase, [Zn(HCOO)₃]-C₂H₈N¹² which is identical to the title compound (**1**), was also yielded from the undesired decomposition of the solvent, DMF. Herein we report the synthesis of [Zn(HCOO)₃] C₂H₈N (**1**) as a major product obtained from 1,4-cyclohexanedicarboxylic acid (chdcH₂) and Zn(NO₃)₂·6H₂O in a mixture of DMF and water through the solvothermal reactions.

RESULTS AND DISCUSSION

The mixture of *trans*-1,4-cyclohexanedicarboxylic acid (chdcH2) and $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in a mixed solvent system (1:0.3, DMF:H₂O) affords colorless crystals of three-dimensional metal-organic framework **1** under the solvothermal conditions. The coordination environment around Zn(II) atom in a secondary building unit can be described as a slightly distorted octahedral with all six positions occupied by symmetrically equivalent formate oxygens, O1, from each half unit of six formate ligands. The coordination sphere of **1** with the atomic numbering scheme is shown in Fig. 1 in which a dimethylammonium cation, $(\text{CH}_3)_2\text{NH}_2^+$, is omitted for clarity. Six crystallographically equivalent deprotonated formic acid moieties link neighboring six different Zn centers through the *anti-anti* coordination mode, giving three-dimensional framework with molecular formula of $[\text{Zn}(\text{HCOO})_3]_n^{n-1}$. The complex **1** contains pores in *ab* crystallographic plane with size of 1.4 Å, however, those pores are occupied by dimethylammonium cations as shown in Fig. 2. The anionic formates and dimethylammonium cations are of the hydrolyzed products of the DMF used as one of the co-solvents. Dimethylformamide is not stable in the presence of strong

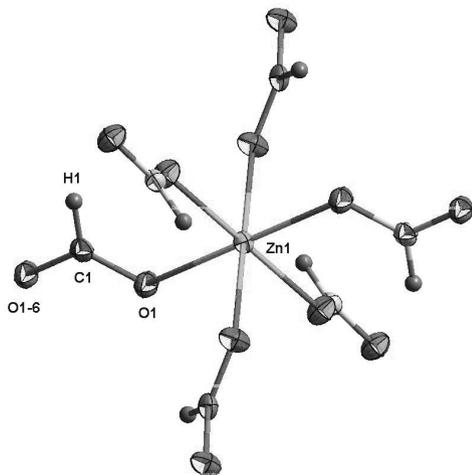


Fig. 1. Coordination sphere around Zn atoms in $[\text{Zn}(\text{HCOO})_3](\text{C}_2\text{H}_8\text{N})$ with ellipsoids drawn at 50% probability level. The disordered dimethyl ammonium cations are omitted for clarity.

bases or strong and is easily hydrolyzed affording the formic acids and dimethylamines, especially at elevated temperatures.¹³

Among the reaction conditions, the temperature would be primary consideration in preparation of the MOFs. If the reaction temperature is too low, it cannot meet the requirements of its reaction kinetics, thus, ligands cannot coordinate to metal ions. On the other hand, if the reaction temperature is too high, it may prevent the formation of the stable structures. In order to investigate an effect of the temperature and an effect of the molar ratio of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to *trans*-1,4-cyclohexanedicarboxylic acid in the formation of **1**, the reaction mixtures in five different molar ratios, 1:1, 1.25:1, 1.5:1, 1.75:1, and 2:1 (metal to ligand), respectively, were heated in only DMF at six different temperatures, 75, 80, 85, 90, 100, and 110 °C, respectively, for 3 days. The title complex **1** was not obtained under all those conditions, instead only round shape opaque microcrystallines were obtained, whose identity could not be characterized by x-ray crystallography because of their limited sizes. Keeping other conditions remaining unchanged except the use of DEF (diethylformide) as the solvent instead of DMF, similar experiments were repeated affording the formation of almost identical products to those of the previous experiments. These results indicate that uses of only DMF or DEF as a solvent are not appropriate choice in the synthesis of **1**.

Further investigation was focused on the use of mixed solvents. The mixtures of one to one molar ratio of $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ to *trans*-1,4-cyclohexane-

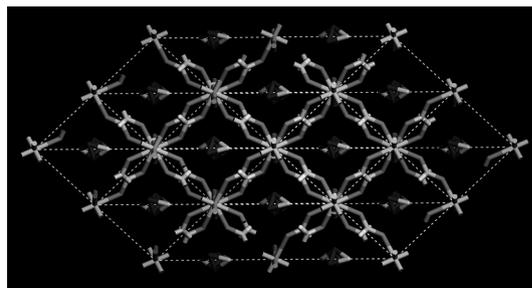


Fig. 2. Layer of $[\text{Zn}(\text{HCOO})_3](\text{C}_2\text{H}_8\text{N})$ showing three-fold disordered dimethylammonium located in the void. Hydrogen atoms are omitted for clarity.

dicarboxylic acid in mixtures of DMF and water (1.0:0.3) were heated at seven temperature points, 65, 70, 75, 80, 85, 90, 100, and 110 °C. From the reactions carried out between 70 °C and 90 °C, colorless cubic shape crystalline **1** were obtained as a major product with small amount of white solids. In the temperature lower than 70 °C, there was no noticeable change in the reaction mixture. On the other hand, only white solids were formed in the temperature higher than 90 °C. In order to confirm the suitable temperatures range suggested from previous experiments, the reaction mixtures with four different molar ratios, 1.25:1, 1.5:1, 1.75:1, and 2:1 (metal to ligand), respectively, in the mixture of DMF and water (1:0.3) were heated at seven different temperatures, 65, 70, 75, 80, 85, 90, 100, and 110 °C respectively, for 3 days. The complex **1** was obtained between 70 °C and 90 °C. Again there was no noticeable change at the lower than 70 °C, and only white solids were formed at the higher than 90 °C. These results indicated that the temperatures range between 70 °C and 90 °C, and DMF/ water solvent system are most suitable reaction conditions for the preparation of **1**.

Because the molar ratio of the metal ions to the ligand can affect the skeleton of MOFs significantly, five reactions with different molar ratios, 1:1, 1.25:1, 1.5:1, 1.75:1, and 2:1, in a mixture of DMF and water (1:0.3), at 80 °C were carried out. From the all five reaction, colorless cubic crystals suitable for x-ray crystallography along with small amount of white solids were obtained. The cell parameters of the colorless cubic crystals obtained were obtained by x-ray crystallography and were compared to each other, showing that these are all identical complex **1**. These results suggest that the molar ratios of the metal ions to the ligand have no significant effects on the preparation of **1**.

Solvent system also can play an important role in the synthesis of MOFs. Keeping molar ratio same (2:1) at 80 °C, seven different volume ratios between DMF and water, 1.2:0.1, 1.1:0.2, 1.0:0.3, 0.9:0.4, 0.8:0.5, 0.7:0.6, and 0.65:0.65, respectively, were used to find the influence of the solvent system. From the reactions with the lower contents

of water compared to that of in 1.0:0.3, the complex **1** was not obtained but small white round opaque solids and small thin colorless fragments. From the reactions with the little higher contents of water (0.9:0.4 and 0.8:0.5), small amount of cloudy cubic crystals was produced with big snowflake white solids. From the reactions with the much higher contents of water (0.7:0.6 and 0.65:0.65), the complex **1** was not obtained at all but big snowflake white solids with small thin colorless fragments. The thin colorless fragments obtained from the co-solvent system, 1.2:0.1, 1.1:0.2, 0.7:0.6 and 0.65:0.65, would be the complexes in which *trans*-1,4-cyclohexanedicarboxylic acids are coordinated to the metal ion, however, unfortunately the size of the fragments was too small for x-ray crystallographic analysis. Keeping all other condition unchanged expect molar ratio between the metal ion and the ligand (1.25:1), seven different volume ratios between DMF and water, 1.2:0.1, 1.1:0.2, 1.0:0.3, 0.9:0.4, 0.8:0.5, 0.7:0.6, and 0.65:0.65, respectively, co-solvent systems in the synthesis of **1** afforded almost identical results as described previously. Only the mixture of DMF and H₂O (1.0:0.3), good quality of the crystals with high yields were obtained. These results indicate that the solvent system employed is critical for the preparation of **1**.

In order to investigate role of the *trans*-1,4-cyclohexanedicarboxylic acid in the decomposition process of DMF, the metal ion, $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, was dissolved in the mixture of DMF and water (1:0.3) and heated at 80 °C in a sealed-glass tube resulting no formation of any solid materials. This result indicates that the ligand, *trans*-1,4-cyclohexanedicarboxylic acid plays important role in the decomposition of DMF at the elevated temperatures and pressures.

CONCLUSION

The present study reported the solvothermal synthesis of an unexpected three-dimensional metal-organic framework, $[\text{Zn}(\text{HCOO})_3](\text{C}_2\text{H}_8\text{N})$ (**1**), as a major product from the reaction between

Zn(NO₃)₂·6H₂O and *trans*-1,4-cyclohexanedicarboxylic acid in the mixture of DMF and H₂O. The title complex **1** was derived from decomposition of the DMF used as the co-solvent. Synthesis of the complex **1** was not affected by the molar ration of the metal ion and the ligand. The reaction temperature and the solvent system, however, play very important role in the formation of **1**.

EXPERIMENTAL SECTION

Materials and methods

All the materials were of a research grade or a spectro-quality grade in the highest purity available and were generally used without further purification. DMF, *trans*-1,4-cyclohexanedicarboxylic acid, and the salts Zn(NO₃)₂·6H₂O were obtained

from Aldrich. Deionized water was obtained by using Milli-Q Advantage A10 Water System from Milipore.

Synthesis of [Zn(HCOO)₃](C₂H₈N).

A mixture of Zn(NO₃)₂·6H₂O (0.0691 g, 2.32 × 10⁻⁴ mol, 2 equivalent), *trans*-1,4-cyclohexanedicarboxylic acid (0.0200g, 1.16 × 10⁻⁴ mol, 1 equivalent) was suspended in a mixture of DMF (1.0 mL) and distilled water (0.3 mL), placed in a sealed glass tube, and heated at 80 °C for 3 days. After cooling to room temperature, the colorless crystalline was obtained, collected by filtration, washed with the mixture of DMF and water, and dried under a reduced pressure at room temperature for 2 h. Anal. Calcd. for [Zn(HCOO)₃](C₂H₈N): C, 24.35; H, 4.46; N, 5.68. Found: C, 24.20; H, 4.32; N, 5.63

Table 1. Crystal data and structure refinement for [Zn(HCOO)₃](C₂H₈N).

Compound	[Zn(HCOO) ₃](C ₂ H ₈ N)	
Color / Shape	colorless / fragment	
Empirical formula	C ₅ H ₁₁ NO ₆ Zn	
Formula weight	246.52	
Temperature	213(2) K	
Crystal system	Trigonal	
Space group	<i>R</i> -3 <i>c</i>	
Unit cell dimensions	<i>a</i> = 8.198(1) Å	<i>α</i> = 90°
	<i>b</i> = 8.198(1) Å	<i>β</i> = 90°
	<i>c</i> = 22.216(4) Å	<i>γ</i> = 120°
Volume	1293.1(3) Å ³	
Z	6	
Density (calculated)	1.899 g/cm ³	
Absorption coefficient	2.848 mm ⁻¹	
Diffractometer / scan	Siemens SMART / CCD area detector	
Radiation / wavelength	Mo <i>K</i> α (graphite monochrom.) / 0.71073 Å	
F(000)	756	
Crystal size	0.20 × 0.20 × 0.20 mm ³	
<i>θ</i> Range for data collection	3.41 to 28.21°	
Index ranges	-10 ≤ <i>h</i> ≤ 8, -10 ≤ <i>k</i> ≤ 10, -15 ≤ <i>l</i> ≤ 29	
Reflections collected	1878	
Independent refls.	350 [R(int) = 0.0401]	
Completeness to <i>θ</i> = 28.21°	98.3 %	
Data / restraints / parameters	350 / 16 / 26	
Goodness-of-fit on <i>F</i> ²	1.087	
Final R indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0434, <i>wR</i> ₂ = 0.1532	
R indices (all data)	<i>R</i> ₁ = 0.0431, <i>wR</i> ₂ = 0.1525	
Extinction coefficient	0.044(6)	
Largest diff. peak and hole	0.412 and -1.183 e/Å	

Table 2. Selected lengths [Å] and angles [°] for [Zn(HCOO)₃](C₂H₈N).

Bond lengths			
Zn(1)-O(1)	2.115(2)	C(1)-O(1)	1.240(3)
N(1S)-C(1S)	1.412(11)		
Bond angles			
O(1)#1-Zn(1)-O(1)#2	91.22(10)	O(1)#1-Zn(1)-O(1)	179.999(1)
O(1)#2-Zn(1)-O(1)	88.78(10)	O(1)-C(1)-O(1)#6	125.9(5)
C(1)-O(1)-Zn(1)	126.9(3)		

Symmetry transformations used to generate equivalent atoms

#1 -x+4/3,-y+2/3,-z+2/3 #2 x-y+1/3,x-1/3,-z+2/3 #3 -x+y+1,-x+1,z #4 y+1/3,-x+y+2/3,-z+2/3 #5 -y+1,x-y,z
#6 -x+2,-x+y+1,-z+1/2 #7 y+1,x-1,-z+1/2

X-ray crystallography

Diffraction intensities for the compound [Zn(HCOO)₃](C₂H₈N) was collected on a Siemens Smart CCD diffractometer with Mo K α monochromated radiation ($\lambda = 0.71073\text{\AA}$) source and a nitrogen cold stream (-75 °C). The data was corrected for Lorentz and polarization effects (SAINT),¹⁴ and semiempirical absorption corrections based on equivalent reflections were applied (SADABS).¹⁵ The structure was solved by direct methods and refined by full-matrix least-squares on F^2 (SHELXTL).¹⁶ All the non-hydrogen atoms were refined anisotropically, and hydrogen atoms were added to their geometrically ideal positions. The cations, C₂H₈N, occupied in the channels, lying on a crystallographic three-fold axis are disordered over three sites. The crystal data and structure refinement are given in Table 1. Selected bond lengths and bond angles are given in Table 2. Crystallographic data have been deposited at the Cambridge Crystallographic Data Centre (CCDC-607093). These data can be obtained free of charge from 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).

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