

# CO<sub>2</sub> Template Synthesis of Metal Formates with a ReO<sub>3</sub> Net

Yun-Qi Tian,\*,† Yu-Ming Zhao,† Hai-Jun Xu,‡ and Cheng-Yu Chi§

Institute of Chemistry for Functionalized Materials, College of Chemistry and Engineering, Liaoning Normal University, Dalian 116029, China, Faculty of Chemical Engineering and Light Industry, Guangdong University of Technology, Guangzhou 510090, China, and School of Materials Science and Engineering, Dalian University of Technology, Dalian 116024, China

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The serendipitous discovery of CO<sub>2</sub> as a template in the fabrication of ferric formate (**1**) has led to the preparation of serial metal(III) formates  $[M^{III}(HCOO)_3 \cdot {}^3/_4CO_2 \cdot {}^1/_4H_2O \cdot {}^1/_4H_COOH ]_{\infty}$  (M = Fe(**1**), AI (**2**), Ga (**3**), and In(**4**)). The X-ray single-crystal determinations showed that the metals have octahedral geometries and are linked by HCOO<sup>-</sup> in the anti–anti style into a 3D ReO<sub>3</sub> net, where CO<sub>2</sub> molecules exist in cages of *mmm* symmetry and are hydrogen bonded to the formic CH groups. An X-ray powder diffraction (XRD) study revealed that **2** is identical to the documented [AI(HCOO)\_3 \cdot xH\_2O]. Further synthetic experiments and <sup>13</sup>C NMR spectroscopy eventually confirmed that **2** should be formulated as [AI(HCOO)\_3 \cdot {}^3/\_4CO\_2 \cdot {}^1/\_4H\_2O \cdot {}^1/\_4HCOOH ]\_{\infty}, which for decades had been mistakenly given as [AI<sup>III</sup>(HCOO)\_3 \cdot xH\_2O].

#### Introduction

Metal—organic frameworks (MOFs) currently are promising materials for applications in catalysis, chirality, conductivity, luminescence, magnetism, sensor, nonlinear optics, and porosity.<sup>1</sup> Thus, the methodology for the preparation of these newly emerging materials has been quickly developed from the primitive stage involving "shake and bake", "mix and wait", and "heat and beat" approaches to rational design and reticular synthesis.<sup>2</sup> Even though for a given metallic cation in the reticular synthesis the geometry of the organic ligand plays an important role in directing the structures, the role of templates is also important because without the templates the predetermined frameworks may not be realized.<sup>3</sup> Usually, the templates used in the synthesis are solvents,<sup>4</sup> organic compounds,<sup>5</sup> or organic/inorganic cations/anions.<sup>6</sup> However, the use of gaseous  $CO_2$  as a template has not been reported

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- <sup>§</sup> Dalian University of Technology.
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to manipulate the synthesis of MOFs because it is always regarded as having a passive role to be fixed, stored, and hosted by organometallic<sup>7</sup> or coordination compounds,<sup>8</sup> porous van der Waals crystals,<sup>9</sup> and coordination polymers<sup>10</sup> or organic hosts.<sup>11</sup> Very recently, we accidently discovered that a ferric formate [Fe<sup>III</sup>(HCOO)<sub>3</sub>·<sup>3</sup>/<sub>4</sub>CO<sub>2</sub>·<sup>1</sup>/<sub>4</sub>H<sub>2</sub>O·<sup>1</sup>/<sub>4</sub>HC-OOH ]<sub>∞</sub> (1) with a ReO<sub>3</sub> net<sup>12</sup> (where Fe replaces Re and (HCOO)<sup>-</sup> replaces O) could be fabricated in the presence

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<sup>\*</sup> To whom correspondence should be addressed. E-mail: yqtian@lnnu.edu.cn.

<sup>&</sup>lt;sup>†</sup> Liaoning Normal University.

Table '	1.	Crystalle	graphic	Parameters
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	1	2	3	4
formula	FeC <sub>4</sub> H <sub>4</sub> O <sub>8.2</sub>	AlC <sub>4</sub> H <sub>4</sub> O <sub>8.25</sub>	$GaC_4H_4O_{8.2}$	InC <sub>4</sub> H <sub>4</sub> O <sub>8.25</sub>
fw	239.92	231.05	253.79	298.90
temperature (K)	293(2)	293(2)	293(2)	293(2)
crystal system	cubic	cubic	cubic	cubic
space group	Im3	Im3	Im3	Im3
cryst. dimensions	$0.2 \times 0.2 \times 0.2$	$0.05 \times 0.05 \times 0.05$	$0.1 \times 0.1 \times 0.1$	$0.1 \times 0.1 \times 0.1$
a (Å)	11.7697(11)	11.4477(6)	11.540(8)	12.161(2)
$V(Å^3)$	1630.4(3)	1500.22(14)	1537.0(19)	1798.5(6)
Z	8	8	8	8
F (000)	912	808	952	1096
$\rho$ (g cm <sup>-3</sup> )	1.861	1.767	2.094	2.123
$\mu (\mathrm{mm}^{-1})$	1.858	0.281	3.590	2.637
R1 $(I > 2\sigma(I))$	0.0798	0.0630	0.0331	0.0593
wR2 $(I > 2\sigma(I)]$	0.1792	0.1763	0.0726	0.1378
R1 (all data)	0.0824	0.0713	0.0501	0.0666
wR2 (all data)	0.1802	0.1841	0.0808	0.1411
GOF	1.104	1.190	1.108	1.245

of gaseous CO<sub>2</sub>, which played the initial role of the template in initiating the generation of the predetermined ReO<sub>3</sub> net. On the basis of this discovery using CO<sub>2</sub> as the template, isostructural metal formates [M<sup>III</sup>(HCOO)<sub>3</sub>·<sup>3</sup>/<sub>4</sub>CO<sub>2</sub>·<sup>1</sup>/<sub>4</sub>H<sub>2</sub>O·<sup>1</sup>/<sub>4</sub>HCOOH ]<sub> $\infty$ </sub> (M = Al (2), Ga (3), and In(4)) have been successfully obtained.

The synthesis of aluminum formate has been studied for more than 70 years<sup>13</sup> because of its wide use in the textile, paper, and pharmaceutical industries and also in ceramics and leather processing. A few forms of aluminum formate have been reported, such as  $[Al(HCOO)_3 \cdot xH_2O]$ ,<sup>13c</sup> [Al-(HCOO)<sub>3</sub>],<sup>13b</sup> and  $[Al(OH)(HCOO)_2 \cdot H_2O]$ .<sup>13b</sup> They have been characterized using IR, NMR spectroscopies and using TGA and XRD, but no X-ray single-crystal study has reported on any of the substances.

Studies of their gallium and indium formate analogues are also rare<sup>14</sup> even though they ought to be excellent precursors of metal oxides. In this article, we report the CO<sub>2</sub> template synthesis of ferric, aluminum(III), gallium(III), and indium-(III) formates 1-4 and their structure characterizations not only with XRD, IR, and <sup>13</sup>C NMR but also with X-ray single-crystal analysis.

#### **Experimental Procedures**

**Materials and Methods.** All of the starting materials were obtained from commercial sources and used without further purification. Elemental analysis of carbon, hydrogen, and nitrogen was carried out with a Perkin-Elmer 240 analyzer. The IR spectroscopy study was performed on a TENSOR 27 FT-IR spectrometer. XRD analysis was undertaken on a Bruker D8 Advance with a Cu K $\alpha$  radiation source ( $\lambda = 0.15418$  nm). Thermal gravimetric analysis (TGA) was performed using a Perkin-Elmer Diamond thermogravimetric analyzer at a heating rate

of 5 °C/min under a flux of air. Solid-state <sup>13</sup>C MAS NMR spectra were recorded on a Bruker Advance 300 apparatus at 300.13 and 75.5 MHz.

Synthesis of Compounds. 1:  $[Fe^{III}_3(\mu-O)(HCOO)_7(H_2O)_2]^{15}$ (0.57 g, 1.0 mmol) and Cu<sup>II</sup>(HCOO)\_2·4H\_2O (0.01 g) were dissolved in 88% formic acid (ca. 30 mL). Then the solution was placed in a Teflon-lined steel autoclave and held at 130 °C for 24 h. The resulting cubic pale-greenish crystals of **1** (which is moisturesensitive) were separated by filtration and dried in a solid-NaOHcontaining desiccator (yield about 41%). Anal. calcd (%) for FeC<sub>4</sub>H<sub>4</sub>O<sub>8.25</sub> (fw 239.92): C 20.02, H 1.68. Found: C 21.02, H 1.72.

**2:** Method A. Al(OH)<sub>3</sub> (0.156 g, 2.0 mmol) (which is confirmed to be gibbsite by XRD analysis) and Na<sub>2</sub>CO<sub>3</sub> (0.424 g, 4.0 mmol) were placed in a Teflon-lined steel autoclave. Then, ca. 30 mL of 88% formic acid was added, and the autoclave was quickly sealed and held at 60 °C for 8 days. The resulting colorless cubic crystals of **2** were separated by filtration and dried in the desiccator (yield about 70%).

**Method B.** Al(OH)<sub>3</sub> (0.39 g, 5.0 mmol) and 30 mL formic acid (88%) were placed in a 250 mL three-necked round-bottomed flask. Then, gaseous CO<sub>2</sub> was bubbled into the reactant, which was heated and refluxed for 24 h. After the reactant was cooled to room temperature, the white powder found in **2** was separated by filtration and washed with anhydrous ethanol (yield about 80%). Anal. calcd (%) for AlC<sub>4</sub>H<sub>4</sub>O<sub>8.25</sub> (fw 231.05): C 20.08, H 1.75. Found: C 20.56, H 1.79.

**3:** Freshly prepared gallium carbonate (ca. 2.0 mmol, which was obtained by the reaction of  $Ga(NO_3)_3$  and  $NaHCO_3$  in water) was added to ca. 40 mL of 88% formic acid. Then, this reactant mixture was left to stand at room temperature for about 24 h. Colorless cubic crystals of **3** were produced and separated by filtration and dried in the desiccator (yield ca. 85%). Anal. calcd (%) for  $GaC_4H_4O_{8.25}$  (fw 253.79): C 18.93, H 1.59. Found: C 19.02, H 1.66.

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<sup>(17)</sup> Indium formate  $[In(CHOO)_3]_{\infty}(4')$ : a = b = 12.5422(7) Å, c = 6.9146(8),  $\alpha = \beta = 90^{\circ}$ ,  $\gamma = 120$ , V = 941.99(13); space group P6<sub>3</sub>. This structure will be reported elsewhere.

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4: The procedure for the preparation of 4 was similar to that for 3, but the single crystal of 4 for X-ray diffraction had to be separated before it had transformed into the more thermodynamically stable needle crystalline 4'. Therefore, the pure bulk product of 4 was not obtained. (The yield of 4' was ca. 88%.)

**X-ray Single-Crystal Crystallography.** The data were collected on a Bruker SMART Apex II CCD system with graphitemonochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 293 K. The structures were solved by direct methods and refined by full-matrix least-squares on  $F^{2,20}$  All non-hydrogen atoms were refined anisotropically. Hydrogen atoms on carbon were generated geometrically and refined isotropically. Although guest formic acid molecules were present in the frameworks of 1–4, they were not initially discovered because of their high lever of disorder. They were later determined by microanalysis, TGA, and <sup>13</sup>C NMR measurements. (The crystal data for 1, 2, 3, and 4 are listed in Table 1.)

## **Results and Discussion**

**Synthesis.** The ferric formate  $[Fe^{III}(HCOO)_3 \cdot {}^3/_4CO_2 \cdot {}^1/_4CO_2 \cdot {}^1$  $_{4}H_{2}O^{1/4}HCOOH ]_{\infty}$  (1) was obtained as we attempted to prepare a mixed-valence coordination polymer of iron formate by reaction 1, where a small amount of copper(I) was working as the catalyst to transform Fe<sup>III</sup> partially into Fe<sup>II</sup>. Given that the CO<sub>2</sub> molecules were guests passively trapped in the framework of ferric formate 1 just like that claimed in a manganese(III) formate<sup>16</sup> (which is an isostructural compound of 1 and whose magnetic properties were studied), we hoped that evacuated 1 could be used as a promising porous material for the selective adsorption and recognition of gaseous CO<sub>2</sub> molecules. However, it was not as we expected. The MOF of 1 free from guest molecules could not be obtained because the TGA of 1 (Supporting Information) showed that its thermal decomposition went with the liberation of the CO<sub>2</sub> molecules. Therefore, it could be deduced that the interactions (hydrogen bonds) between the  $CO_2$  molecules and the framework of 1 are so strong (with a hydrogen bond length 2.665 Å) that  $CO_2$  may be seen as an unmovable template supporting the [Fe<sup>III</sup>(H-COO)<sub>3</sub>]∞ framework other than solely as a guest trapped in the framework. (It was lately confirmed that the hydrogen bond lengths in 2, 3, and 4 are 2.459, 2.575, and 2.911 Å, respectively. With the longest hydrogen bonds, 4 has the weakest interactions between CO2 and its unstable framework). Provided the CO<sub>2</sub> functions as an unmovable template in generating ferric formate 1, some metal(III) (with octahedral geometry) formates may also generate the ReO<sub>3</sub> net under the template effect of gaseous CO<sub>2</sub> molecules. Thus, the synthesis of aluminum(III), gallium(III), and indium(III) formates with the ReO<sub>3</sub> net becomes a criterion for verifying the template role of CO<sub>2</sub> molecules. Moreover, it also provides a pathway to the unprecedented gallium(III) and indium(III) formates.

$$[Fe(\mu-O)(HCOO)_{7}(H_{2}O)_{2}]^{[15]} + HCOOH \xrightarrow{Cu^{II}} 2Fe^{II} + Fe^{III} + 5HCOO^{-} + CO_{2} + 3H_{2}O (1)$$
$$Fe(HCOO)_{3} \cdot \sqrt[3]{4}CO_{2} \cdot \sqrt[1]{4}HCOOH \cdot \sqrt[1]{4}H_{2}O (1)$$

$$\begin{bmatrix} 2Cu^{II} + HCOOH \rightarrow 2Cu^{I} + CO_{2} + H_{2}O \\ Cu^{I} + Fe^{III} \rightarrow Cu^{II} + Fe^{II} \end{bmatrix}$$

The synthesis of aluminum formate **2** was carried out under solvothermal conditions by the reactions of Al(OH)<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub> with 88% formic acid in a sealed autoclave, whereas the preparation of gallium formate **3** and indium formate **4** was conducted by the reactions of a freshly prepared gallium/indium carbonate with formic acid at room temperature. Metal formates **2**, **3**, and **4** were all obtained as colorless cubic crystals. However, a single phase of bulk **4** was not acquired because it soon transformed into a needle crystalline solid formulated as  $[In^{II}(HCOO)_3]_{\infty}$  (**4**').<sup>17</sup>

To reconfirm the CO<sub>2</sub> template effect, we refluxed a reactant mixture of Al(OH)<sub>3</sub> and formic acid in a CO<sub>2</sub> atmosphere that gave rise to **2** with a sufficient reaction time (Figure 1a). However, as we conducted the reaction in an argon atmosphere, it generated [Al(OH)(HCOO)<sub>2</sub>·H<sub>2</sub>O] (Figure 1b), which is consistent with the result observed by Chaplygina.<sup>13b-d</sup> Moreover, as the reaction was performed in a sealed autoclave containing air with insufficient CO<sub>2</sub> for the reaction, it produced a mixture of [Al(OH)(HCOO)<sub>2</sub>·H<sub>2</sub>O] and **2** that tallies with the result given in ref 13b if **2** is taken as the so-called [Al(HCOO)<sub>3</sub>·xH<sub>2</sub>O]. Thus, the above reactions can be summarized as a reaction 2 where the template role of CO<sub>2</sub> has been experimentally confirmed.

$$AI(OH)_{3} + 2HCOOH \rightarrow [AI(OH)(HCOO)_{2} \cdot H_{2}O] \qquad (2-1)$$
$$[AI(OH)(HCOO)_{2} \cdot H_{2}O] \xrightarrow{CO_{2}}$$
$$[AI(HCOO)_{3} \cdot {}^{3}/_{4}CO_{2} \cdot {}^{1}/_{4}H_{2}O \cdot {}^{1}/_{4}HCOOH] (2-2)$$

Crystal Structure. X-ray single-crystal analyses revealed that metal(III) formates 1-4 are isostructural. They crystallize cubically with space group Im3. Each of its unit cells contains eight metals that are coordinated with six oxygen atoms of six formate ligands in an anti-anti bridging mode<sup>18</sup> just like the structure of Prussian blue with the ReO<sub>3</sub> net. The metal(III) formates demonstrate very open frameworks in which guest H<sub>2</sub>O and CO<sub>2</sub> molecules are accommodated. In the unit cell in Figure 2, which is used to help describe the number and the location of the guest molecules, there are two H<sub>2</sub>O and six CO<sub>2</sub> molecules. The H<sub>2</sub>O molecules are located at the center and corner points of the unit cell and in the voids of cage A with m3 symmetry; the CO<sub>2</sub> molecules lie at the centers of the planes and the edges of the unit cell, they are in the rooms of cage B with mmm symmetry, and they are hydrogen bonded to the CH groups of the  $[M^{III}(HCOO)_3]_{\infty}$  frameworks. In MOFs 1–4, the C–O bond lengths in  $CO_2$  are all approximately 1.2 (0) Å, whereas the hydrogen bonds (CH···O-C-O) are 2.7(0), 2.5(0), 2.6-(0), and 2.9(0) Å. (The metal-metal distances are 5.89(1),

<sup>(20)</sup> SHELXTL NT ver. 5.1 Installation and Release Notes April 7, 1998.



**Figure 1.** XRD patterns of substances related to reaction 2: (a<sub>1</sub>) the reactant Al(OH)<sub>3</sub> (gibbsite); (a<sub>2</sub>) the product of reaction 2 lasting for 5 h; (a<sub>3</sub>) the product of reaction 2 lasting for 14 h; (a<sub>4</sub>) the product of reaction 2 lasting for 24 h; (b<sub>1</sub>) the documented XRD of [Al(OH)(HCOO)<sub>2</sub>·H<sub>2</sub>O] (ICDD no. 37-771); (b<sub>2</sub>) the product of reaction 2-1 in an argon atmosphere lasting for 24 h; (c) the product of reaction 2-1 in a sealed autoclave for 24 h (#, the phase of **2**;  $\theta$ , the phase of [Al(OH)(CHOO)<sub>2</sub>·H<sub>2</sub>O); \*, the phase of unreacted Al(OH)<sub>3</sub>].

5.72(1), 5.77(1), and 6.08(1), respectively.) Obviously, the interactions (hydrogen bonds) between CO<sub>2</sub> and the MOF in **4** are the weakest among the metal formate isostructures. Therefore, it is reasonable for **4** to liberate CO<sub>2</sub> and to transform into indium formate **4'**. There are also guest formic acid molecules accommodated in the MOFs of **1**–**4** that were confirmed by <sup>13</sup>C MAS NMR and IR spectroscopies, and microanalyses. These formic acids may be accommodated in cage A, but they evaded X-ray analysis as a result of their high level of disorder.

**X-ray Powder Diffraction (XRD).** The XRD patterns of bulk solids 1-3 completely agree with those simulated from the data of their single-crystal analyses (Figure 3b,c). More intriguing is that the XRD pattern of **2** is consistent with that of the documented [Al(HCOO)<sub>3</sub>•*x*H<sub>2</sub>O] (ICDD no. 38-655)<sup>13c</sup> (Figure 3a). Obviously, the two formulas represent the same substance but indicate two possibilities: either the quantities of CO<sub>2</sub> and HCOOH in **2** (also in **1**, **3**, and **4**) might be so small that its formula could be approximated to [Al(HCOO)<sub>3</sub>•*x*H<sub>2</sub>O], or aluminum formate **2** had been mistaken for [Al(HCOO)<sub>3</sub>•*x*H<sub>2</sub>O] ever since it was discovered. The key to resolving this question had to be confirmation of the existence of CO<sub>2</sub> molecules in the bulk products



**Figure 2.** View of the crystal unit cell of the metal(III) formates (Fe(1), Al(2), Ga(3), and In(4)). Selected distances (Å) and angles (deg), 1: Fe1–O1 1.989(3), C1–O1 1.244(3), C2–O2 1.182(4), H1····O2 2.665(3); O1–C1–O1 124.56(4), O2–C2–O2 180.00(1). **2**: Al1–O1 1.887(2), C1–O1 1.250(6), C2–O2 1.193(5), H1···O2 2.459(4); O1–C1–O1 122.26(4), O2–C2–O2 179.99(1). **3**: Ga1–O1 1.953(1), C1–O1 1.244(1), C2–O2 1.197-(1), H1···O2 2.575(1); O1–C1–O1 122.11(2), O2–C2–O2 179.98(4). **4**: In1–O1 2.122(2), C1–O1 1.239(2), C2–O2 1.179(3), H1···O2 2.911(1); O1–C1–O1 124.94(1), O2–C2–O2 179.98(1).



**Figure 3.** (a) Documented XRD for the so-called  $[Al(HCOO)_3 \cdot xH_2O]$  (ICDD no. 38-655). (b) XRD pattern of the bulk sample of **2**. (c) XRD pattern simulated from the single-crystal data of **2**.

of 1-4. Therefore, solid-state <sup>13</sup>C NMR spectra were measured for 2, 3, and 4'.

**Solid-State** <sup>13</sup>C **NMR.** The <sup>13</sup>C MAS NMR spectra (Figure 4) of **2** and **3** are similar to each other. In addition to the signals of matrix carbon atoms in the framework of **2** and **3** at  $\delta = 175.1$  and 176.1 respectively, signals of CO<sub>2</sub> appear at  $\delta = 157.3$  in **2** and  $\delta = 157.1$  in **3**, whereas signals of formic acid (FA) appear at  $\delta = 163.3$  in **2** and  $\delta = 163.9$  in **3**, respectively. The <sup>13</sup>C NMR spectrum of **4'** reveals a single signal at  $\delta = 174.0$  assigned to the matrix carbon atoms of the framework. The IR spectra of **1**–**3** also indicate the existence of CO<sub>2</sub> in the frameworks because the  $\nu_{O=C=O}$  peaks at ca. 2344 and 2361 cm<sup>-1</sup> appear in **1**–**3** but not in **4'**. Thus, the existence of CO<sub>2</sub> and formic acid in **2** and **3** (and also in **1** and **4**) has been confirmed, and formula [Al-(HCOO)<sub>3</sub>·xH<sub>2</sub>O] documented in the literature should be corrected to [Al<sup>III</sup>(HCOO)<sub>3</sub>·3/<sub>4</sub>CO<sub>2</sub>·1/<sub>4</sub>H<sub>2</sub>O·1/<sub>4</sub>HCOOH ]<sub>∞</sub> (**2**).

Compared with the <sup>13</sup>C NMR of CO<sub>2</sub> dissolved in deuterated THF with its resonance signal at  $\delta = 125.8$ ,<sup>19</sup> stored in porous van der Waals crystals at  $\delta = 133.3^9$  and accommodated in an organic host at  $\delta = 127.1$ ,<sup>11</sup> the <sup>13</sup>C NMR signal of CO<sub>2</sub> in **2** or **3** at  $\delta \approx 157$  is largely downfield



Figure 4. Fast magic-angle spinning  $^{13}$ C NMR of 2 (bottom), 3 (middle), and 4' (top).

shifted, but it is closer to  $\delta = 145$ , the <sup>13</sup>C NMR resonance of free CO<sub>2</sub> at liquid-nitrogen temperature.<sup>8</sup> Therefore, the considerable downfield shift of the carbon resonance of CO<sub>2</sub> in **2** or **3** does not only come from the electronic shielding of the MOFs; it may also come from the loss of molecular movement in the MOFs. The <sup>13</sup>C NMR spectrum for the socalled [Al(HCOO)<sub>3</sub>•*x*H<sub>2</sub>O] was claimed to have been measured in ref 13d, where the  $\delta = 165$  signal was assigned to the formate ligands coordinated to the aluminum atoms. However, as a coordination polymer actually formulated as [Al<sup>III</sup>(HCOO)<sub>3</sub>•<sup>3</sup>/<sub>4</sub>CO<sub>2</sub>•<sup>1</sup>/<sub>4</sub>H<sub>2</sub>O•<sup>1</sup>/<sub>4</sub>HCOOH ]<sub>∞</sub>, which is insoluble in CDCl<sub>3</sub>, the signal  $\delta = 165$  should have been assigned to the carbon of the guest formic acid distributed in the 3D framework of **2** and subsequently extracted into the CDCl<sub>3</sub> solvent in the <sup>13</sup>C NMR measurement.

### Conclusions

We have reported the serendipitous discovery of CO<sub>2</sub> as a template in manipulating the MOF synthesis that has led to the generation of serial metal(III) formates with a ReO<sub>3</sub> net. On the basis of X-ray single-crystal analyses and XRD, IR, and <sup>13</sup>C NMR analyses, we not only have confirmed the template role of gaseous CO<sub>2</sub> molecules in the metal formate synthesis of 1-4 but also have corrected a mistake in the literature (ref 13) in which the aluminum formate formulated as [Al<sup>III</sup>(HCOO)<sub>3</sub>·<sup>3</sup>/<sub>4</sub>CO<sub>2</sub>·<sup>1</sup>/<sub>4</sub>H<sub>2</sub>O·<sup>1</sup>/<sub>4</sub>HCOOH ]<sub>∞</sub> was mistakenly formulated as [Al(HCOO)<sub>3</sub>·xH<sub>2</sub>O]. From this result, it can now be seen why the product of a pure and highly crystallized aluminum formate was so difficult to prepare in the past. And the discussion<sup>13d</sup> on the results from the reaction of Al(OH)<sub>3</sub> with HCOOH can now be settled. Also, this unprecedented CO<sub>2</sub> template synthesis has led to unprecedented gallium formate 3 and indium formate 4, which should be excellent precursors of metal oxides.

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**Supporting Information Available:** Crystallographic data in CIF format and IR spectroscopy, XRD, and TEM image of aluminum formate. This material is available free of charge via the Internet at http://pubs.acs.org.

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