Inorg. Chem. **2007**, *46*, 1612–1616

Inorganic Chemistry
Article

CO_2 Template Synthesis of Metal Formates with a ReO_3 Net

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Received September 12, 2006

The serendipitous discovery of CO_2 as a template in the fabrication of ferric formate (**1**) has led to the preparation of serial metal(III) formates $[\mathrm{M^{III}(HCOO)_3\cdot{}^3/_4CO_2\cdot{}^1/_4H_2O\cdot{}^1/_4HCOOH}]_\infty$ (M = Fe(**1**), Al (**2**), Ga (**3**), and In(**4**)). The X-ray single-crystal determinations showed that the metals have octahedral geometries and are linked by $HCOO^-$ in the anti–anti style into a 3D ReO_3 net, where CO_2 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 $[\mathrm{Al(HCOO)_3\cdot}x\mathrm{H_2O}]$. Further synthetic experiments and ^{13}C NMR spectroscopy eventually confirmed that **2** should be formulated as $[\mathrm{Al(HCOO)_3\cdot{}^3/_4CO_2\cdot{}^1/_4H_2O\cdot{}^1/_4HCOOH}]_\infty$, which for decades had been mistakenly given as $[\mathrm{Al^{III}(HCOO)_3\cdot}x\mathrm{H_2O}]$.

Introduction

Metal–organic frameworks (MOFs) currently are promising materials for applications in catalysis, chirality, conductivity, luminescence, magnetism, sensor, nonlinear optics, and porosity.[1] 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.[2] 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.[3] Usually, the templates used in the synthesis are solvents,[4] organic compounds,[5] or organic/inorganic cations/anions.[6] However, the use of gaseous CO_2 as a template has not been reported to manipulate the synthesis of MOFs because it is always regarded as having a passive role to be fixed, stored, and hosted by organometallic[7] or coordination compounds,[8] porous van der Waals crystals,[9] and coordination polymers[10] or organic hosts.[11] Very recently, we accidently discovered that a ferric formate $[\mathrm{Fe^{III}(HCOO)_3\cdot{}^3/_4CO_2\cdot{}^1/_4H_2O\cdot{}^1/_4HCOOH}]_\infty$ (**1**) with a ReO_3 net[12] (where Fe replaces Re and $(HCOO)^-$ replaces O) could be fabricated in the presence

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10.1021/ic0617240 CCC: $37.00

Table 1. Crystallographic Parameters

	1	**2**	**3**	**4**
formula	$FeC_4H_4O_{8.2}$	$AlC_4H_4O_{8.25}$	$GaC_4H_4O_{8.2}$	$InC_4H_4O_{8.25}$
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	$Im\bar{3}$	$Im\bar{3}$	$Im\bar{3}$	$Im\bar{3}$
cryst. dimensions	0.2 × 0.2 × 0.2	0.05 × 0.05 × 0.05	0.1 × 0.1 × 0.1	0.1 × 0.1 × 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
ρ (g cm^{-3})	1.861	1.767	2.094	2.123
μ (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_2, which played the initial role of the template in initiating the generation of the predetermined ReO_3 net. On the basis of this discovery using CO_2 as the template, isostructural metal formates $[M^{III}(HCOO)_3{\cdot}{}^3/_4CO_2{\cdot}{}^1/_4H_2O{\cdot}{}^1/_4HCOOH\ ]_\infty$ (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[13] 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 $[Al(HCOO)_3{\cdot}xH_2O]$,[13c] $[Al(HCOO)_3]$,[13b] and $[Al(OH)(HCOO)_2{\cdot}H_2O]$.[13b] 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[14] even though they ought to be excellent precursors of metal oxides. In this article, we report the CO_2 template synthesis of ferric, aluminum(III), gallium(III), and indium(III) formates **1**−**4** and their structure characterizations not only with XRD, IR, and ^{13}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 Kα 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 ^{13}C MAS NMR spectra were recorded on a Bruker Advance 300 apparatus at 300.13 and 75.5 MHz.

Synthesis of Compounds. 1: $[Fe^{III}_3(\mu\text{-}O)(HCOO)_7(H_2O)_2]$[15]-(0.57 g, 1.0 mmol) and $Cu^{II}(HCOO)_2{\cdot}4H_2O$ (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 moisture-sensitive) were separated by filtration and dried in a solid-NaOH-containing desiccator (yield about 41%). Anal. calcd (%) for $FeC_4H_4O_{8.25}$ (fw 239.92): C 20.02, H 1.68. Found: C 21.02, H 1.72.

2: Method A. $Al(OH)_3$ (0.156 g, 2.0 mmol) (which is confirmed to be gibbsite by XRD analysis) and Na_2CO_3 (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. $Al(OH)_3$ (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_2 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 $AlC_4H_4O_{8.25}$ (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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(17) Indium formate $[In(CHOO)_3]_\infty$(**4′**) : $a = b = 12.5422(7)$ Å, $c = 6.9146(8)$, $\alpha = \beta = 90°$, $\gamma = 120$, $V = 941.99(13)$; space group $P6_3$. 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 graphite-monochromated Mo Kα 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 ^{13}C NMR measurements. (The crystal data for **1**, **2**, **3**, and **4** are listed in Table 1.)

Results and Discussion

Synthesis. The ferric formate $[\mathrm{Fe^{III}(HCOO)_3{\cdot}{}^3/_4CO_2{\cdot}{}^1/_4H_2O{\cdot}{}^1/_4HCOOH}]_\infty$ (**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 $\mathrm{Fe^{III}}$ partially into $\mathrm{Fe^{II}}$. Given that the CO_2 molecules were guests passively trapped in the framework of ferric formate **1** just like that claimed in a manganese(III) formate[16] (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_2 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_2 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 $[\mathrm{Fe^{III}(HCOO)_3}]_\infty$ 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 CO_2 and its unstable framework). Provided the CO_2 functions as an unmovable template in generating ferric formate **1**, some metal(III) (with octahedral geometry) formates may also generate the ReO_3 net under the template effect of gaseous CO_2 molecules. Thus, the synthesis of aluminum(III), gallium(III), and indium(III) formates with the ReO_3 net becomes a criterion for verifying the template role of CO_2 molecules. Moreover, it also provides a pathway to the unprecedented gallium(III) and indium(III) formates.

$$[\mathrm{Fe}(\mu{-}\mathrm{O})(\mathrm{HCOO})_7(\mathrm{H_2O})_2]^{[15]} + \mathrm{HCOOH} \xrightarrow[\text{solvothermal}]{\mathrm{Cu^{II}}} 2\mathrm{Fe^{II}} + \mathrm{Fe^{III}} + 5\mathrm{HCOO^-} + \mathrm{CO_2} + 3\mathrm{H_2O} \quad (1)$$

$$\mathrm{Fe(HCOO)_3{\cdot}{}^3/_4CO_2{\cdot}{}^1/_4HCOOH{\cdot}{}^1/_4H_2O}\ (\mathbf{1})$$

$$\begin{bmatrix} 2\mathrm{Cu^{II}} + \mathrm{HCOOH} \rightarrow 2\mathrm{Cu^{I}} + \mathrm{CO_2} + \mathrm{H_2O} \\ \mathrm{Cu^{I}} + \mathrm{Fe^{III}} \rightarrow \mathrm{Cu^{II}} + \mathrm{Fe^{II}} \end{bmatrix}$$

The synthesis of aluminum formate **2** was carried out under solvothermal conditions by the reactions of $Al(OH)_3$ and Na_2CO_3 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 $[\mathrm{In^{III}(HCOO)_3}]_\infty$ (**4′**).[17]

To reconfirm the CO_2 template effect, we refluxed a reactant mixture of $Al(OH)_3$ and formic acid in a CO_2 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 $[\mathrm{Al(OH)(HCOO)_2{\cdot}H_2O}]$ (Figure 1b), which is consistent with the result observed by Chaplygina.[13b−d] Moreover, as the reaction was performed in a sealed autoclave containing air with insufficient CO_2 for the reaction, it produced a mixture of $[\mathrm{Al(OH)(HCOO)_2{\cdot}H_2O}]$ and **2** that tallies with the result given in ref 13b if **2** is taken as the so-called $[\mathrm{Al(HCOO)_3{\cdot}}x\mathrm{H_2O}]$. Thus, the above reactions can be summarized as a reaction 2 where the template role of CO_2 has been experimentally confirmed.

$$\mathrm{AI(OH)_3} + 2\mathrm{HCOOH} \rightarrow [\mathrm{AI(OH)(HCOO)_2{\cdot}H_2O}] \qquad (2\text{-}1)$$

$$[\mathrm{AI(OH)(HCOO)_2{\cdot}H_2O}] \xrightarrow{\mathrm{CO_2}} [\mathrm{AI(HCOO)_3{\cdot}{}^3/_4CO_2{\cdot}{}^1/_4H_2O{\cdot}{}^1/_4HCOOH}] \quad (2\text{-}2)$$

Crystal Structure. X-ray single-crystal analyses revealed that metal(III) formates **1**−**4** are isostructural. They crystallize cubically with space group $Im\bar{3}$. 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[18] just like the structure of Prussian blue with the ReO_3 net. The metal(III) formates demonstrate very open frameworks in which guest H_2O and CO_2 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_2O and six CO_2 molecules. The H_2O molecules are located at the center and corner points of the unit cell and in the voids of cage A with $m\bar{3}$ symmetry; the CO_2 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 $[\mathrm{M^{III}(HCOO)_3}]_\infty$ 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),

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[20] *SHELXTL NT* ver. 5.1 Installation and Release Notes April 7, 1998.

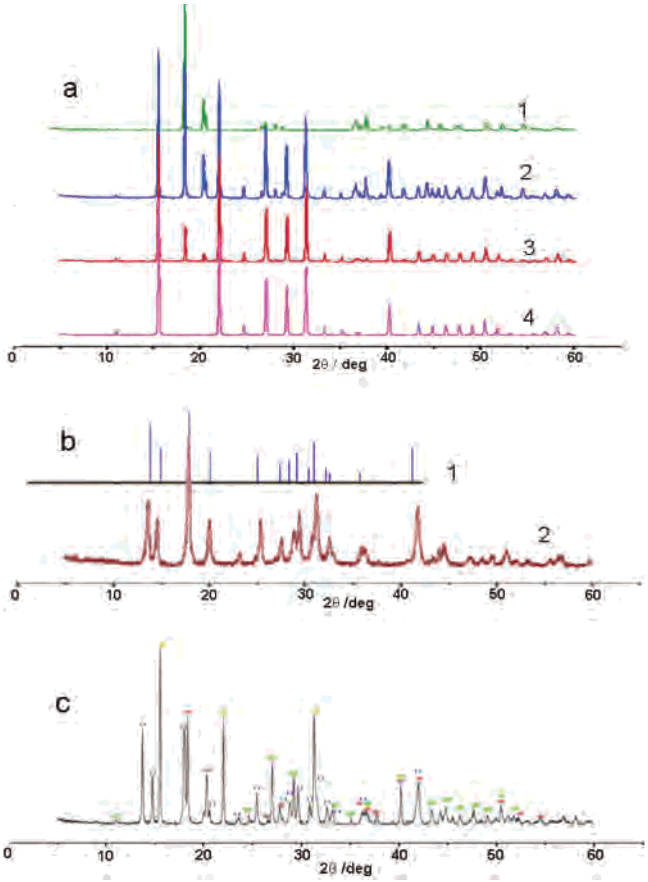

Figure 1. XRD patterns of substances related to reaction 2: (a_1) the reactant $Al(OH)_3$ (gibbsite); (a_2) the product of reaction 2 lasting for 5 h; (a_3) the product of reaction 2 lasting for 14 h; (a_4) the product of reaction 2 lasting for 24 h; (b_1) the documented XRD of $[Al(OH)(HCOO)_2{\cdot}H_2O]$ (ICDD no. 37-771); (b_2) 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**; θ, the phase of $[Al(OH)(CHOO)_2{\cdot}H_2O)$; *, the phase of unreacted $Al(OH)_3$)].

5.72(1), 5.77(1), and 6.08(1), respectively.) Obviously, the interactions (hydrogen bonds) between CO_2 and the MOF in **4** are the weakest among the metal formate isostructures. Therefore, it is reasonable for **4** to liberate CO_2 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 ^{13}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 $[Al(HCOO)_3{\cdot}xH_2O]$ (ICDD no. 38-655)[13c] (Figure 3a). Obviously, the two formulas represent the same substance but indicate two possibilities: either the quantities of CO_2 and HCOOH in **2** (also in **1**, **3**, and **4**) might be so small that its formula could be approximated to $[Al(HCOO)_3{\cdot}xH_2O]$, or aluminum formate **2** had been mistaken for $[Al(HCOO)_3{\cdot}xH_2O]$ ever since it was discovered. The key to resolving this question had to be confirmation of the existence of CO_2 molecules in the bulk products of **1**−**4**. Therefore, solid-state ^{13}C NMR spectra were measured for **2**, **3**, and **4′**.

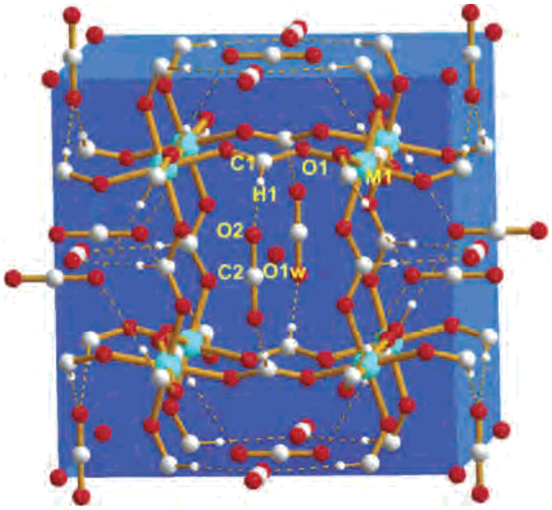

Figure 2. View of the crystal unit cell of the metal(III) formates (Fe(**1**), Al(**2**), Ga(**3**), and In(**4**)). Selected distances (Å) and angles (deg), **1**: Fe1−O1 1.989(3), C1−O1 1.244(3), C2−O2 1.182(4), H1···O2 2.665(3); O1−C1−O1 124.56(4), O2−C2−O2 180.00(1). **2**: Al1−O1 1.887(2), C1−O1 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).

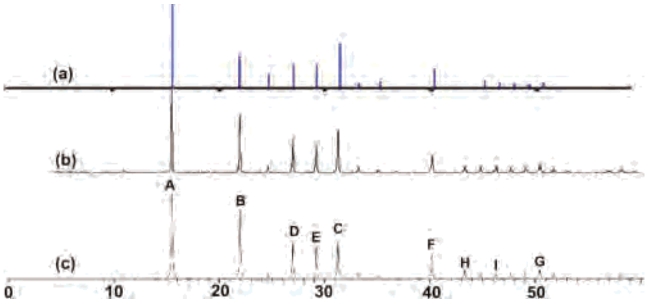

Figure 3. (a) Documented XRD for the so-called $[Al(HCOO)_3{\cdot}xH_2O]$ (ICDD no. 38-655). (b) XRD pattern of the bulk sample of **2**. (c) XRD pattern simulated from the single-crystal data of **2**.

Solid-State ^{13}C NMR. The ^{13}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_2 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 ^{13}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_2 in the frameworks because the $\nu_{O=C=O}$ peaks at ca. 2344 and 2361 cm^{-1} appear in **1**−**3** but not in **4′**. Thus, the existence of CO_2 and formic acid in **2** and **3** (and also in **1** and **4**) has been confirmed, and formula $[Al(HCOO)_3{\cdot}xH_2O]$ documented in the literature should be corrected to $[Al^{III}(HCOO)_3{\cdot}{}^3/_4CO_2{\cdot}{}^1/_4H_2O{\cdot}{}^1/_4HCOOH\,]_\infty$ (**2**).

Compared with the ^{13}C NMR of CO_2 dissolved in deuterated THF with its resonance signal at $\delta = 125.8$,[19] stored in porous van der Waals crystals at $\delta = 133.3$[9] and accommodated in an organic host at $\delta = 127.1$,[11] the ^{13}C NMR signal of CO_2 in **2** or **3** at $\delta \approx 157$ is largely downfield

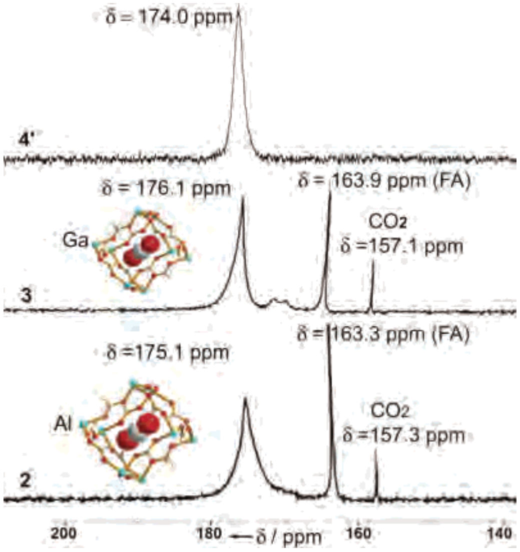

Figure 4. Fast magic-angle spinning ^{13}C NMR of **2** (bottom), **3** (middle), and **4′** (top).

shifted, but it is closer to $\delta = 145$, the ^{13}C NMR resonance of free CO_2 at liquid-nitrogen temperature.[8] Therefore, the considerable downfield shift of the carbon resonance of CO_2 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 ^{13}C NMR spectrum for the so-called $[Al(HCOO)_3 \cdot xH_2O]$ 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 $[Al^{III}(HCOO)_3 \cdot {}^3/_4CO_2 \cdot {}^1/_4H_2O \cdot {}^1/_4HCOOH\ ]_\infty$, which is insoluble in $CDCl_3$, 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 $CDCl_3$ solvent in the ^{13}C NMR measurement.

Conclusions

We have reported the serendipitous discovery of CO_2 as a template in manipulating the MOF synthesis that has led to the generation of serial metal(III) formates with a ReO_3 net. On the basis of X-ray single-crystal analyses and XRD, IR, and ^{13}C NMR analyses, we not only have confirmed the template role of gaseous CO_2 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 $[Al^{III}(HCOO)_3 \cdot {}^3/_4CO_2 \cdot {}^1/_4H_2O \cdot {}^1/_4HCOOH\ ]_\infty$ was mistakenly formulated as $[Al(HCOO)_3 \cdot xH_2O]$. 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[13d] on the results from the reaction of $Al(OH)_3$ with HCOOH can now be settled. Also, this unprecedented CO_2 template synthesis has led to unprecedented gallium formate **3** and indium formate **4**, which should be excellent precursors of metal oxides.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (no. 20571013).

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.

IC0617240