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Role of Temperature and Time in the Formation of Infinite −M−O−M− Linkages and Isolated Clusters in MOFs: A Few Illustrative Examples

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The role of temperature and time of reaction in the formation of metal−organic frameworks (MOFs) has been studied in two systems of compounds, manganese oxybis(benzoate) and manganese trimellitates, and the results compared and contrasted with other similar studies in the literature. The investigation reveals the formation of six different phases in oxybis(benzoate) and three phases in trimellitate systems. The low-temperature phases in both systems of compounds possess Mn_4 cluster units linked by the carboxylate ligands, while the high-temperature phase, irrespective of the duration of the reaction, has a three-dimensional structure with −Mn−O−Mn− linkages with brucite-related layers pillared by oxybis(benzoate) and Kagome-related layers pillared by trimellitate ligands. In all of the preparation, the reactions appear to have thermodynamic control as a function of the temperature. The isolation of low-dimensional structures in manganese oxybis(benzoate) at moderate time and temperature indicates possible kinetic control. The formation of reactive low-dimensional phases has been rationalized by considering the local charge distribution around the Mn site and also invoking a possible dissolution−recrystalization mechanism.

Introduction

Metal−organic framework (MOF) compounds have attracted considerable attention because of their unique structures that combine the coordination versatility of the metal ion and the multibinding modes of the organic ligands. The relatively easier possibility of tuning the pore sizes, the introduction of functionality, and their possible use in catalysis, sorption, separation, and related processes have provided the much required impetus to study this class of materials. Intense research activity during the past decade or so has resulted in the isolation of many MOF compounds of varying composition and structure.[1] The diversity exhibited by these compounds stands as a testimony to the usefulness of the strong directional coordination bonds and the control achieved in the design of predetermined frameworks.[2] Some of the MOF compounds, thus prepared, exhibit good host−guest properties indicating remarkable structural robustness and flexibility, very large pore volume and surface area, etc.[3]

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Recently, there has been some effort to prepare MOFs based on a reticular synthesis approach.[4] Thus, designed organic linkers have been employed as "struts" or bridges to connect the metal centers, forming new compounds with interesting adsorption properties.[5] In spite of these developments, our understanding of the formation of such compounds continues to be poor. One of the persistent issues with respect to the synthesis of framework solids is that their formation appears to be more kinetically driven rather than based on thermodynamic control. Thus, it may be possible to isolate many kinetically favored interesting new structures enroute to the thermodynamically favored stable ones. Thus, the *trial and error* approach appears to be more appealing to study the formation of extended framework structures. In light of this, it may be worth noting that a reactive intermediate, based on a simple four-membered ring (zero-dimensional), has been isolated in the family of zinc phosphates and shown to be reactive, giving rise to structures of higher dimensionality.[6] Studies of this nature are not many on the MOF compounds because the focus appears to be more on understanding the role of organic ligands such as carboxylates, amines, etc.[7] Intense research activity over the years, however, has provided examples of MOFs with more than two structures formed with the same combination of metal and organic ligands.[8]

Mechanistic studies, especially on the formation of solids with extended structures, are difficult to perform because of the large number of variables involved in the synthesis. Systematic studies on the role of simple variables such as the temperature and time of the reaction can be investigated, although such studies are rare.[8b,9] One of the emerging trends in the area of MOFs appears to be the study of the possible competition between the thermodynamic and kinetic factors in the formation of such structures. There have been some studies toward this direction, which indicates that in some cases the thermodynamic considerations appear to be more important than the kinetic ones. Cheetham and co-workers provided the first insight on the influence of the reaction temperature during the formation of cobalt succinate phases, which indicated the formation of denser higher dimensional structures with extended −M−O−M− connectivity upon an increase in the the reaction temperature, through an entropy-driven dehydration pathway.[10] It has been shown that compounds with extended −M−O−M− connectivity also have higher thermal stability as well.[11] A similar trend was also observed by Kitagawa and co-workers during their study of the formation of cobalt pyridinedicarboxylates.[12] Here a two-dimensional hydrated structure at low temperature gives way to a three-dimensional structure with infinite one-dimensional −M−O−M− linkages at higher temperatures. In a related study, the use of temperature and composition as the variables gave rise to three different homochiral cadmium camphorates.[13] Postsynthesis modification studies have been carried out, which also establishes the importance of temperature in the control of dimensionality in nickel diphosphonate structures.[14] During the course of our studies toward the understanding of the formation of structures with extended networks, we have recently reported the role of temperature in the formation of manganese oxybis(benzoate) structures.[15] In a continuation of this theme, we have taken up the study of manganese-based MOF compounds prepared using two different aromatic poly(carboxylic acids), 4,4′-oxybis(benzoic acid) (OBA), and trimellitic acid (1,2,4-benzenetricarboxylic acid, BTC). In this paper, we present a brief overview of the role of time and temperature of reaction in the formation of MOFs along with our findings on the manganese benzenecarboxylate phases.

Experimental Section

Materials. The reagents needed for the synthesis of the compounds are $Mn(OAC)_2 \cdot 4H_2O$ [Ranbaxy (Gurgaon, India), 99%], 4,4′-oxybis(benzoic acid), 1,2,4-benzenetricarboxylic acid [Lancaster (Lancaster, U.K.), 99%], imidazole [Ranbaxy (Gurgaon, India), 99%], and KOH [CDH (New Delhi, India), 99%]. The water used was double distilled through a Millipore membrane.

(a) Synthesis of Mn-OBA Compounds. A typical reaction mixture containing $Mn(OAc)_2 \cdot 4H_2O$ (0.245 g, 1 mM), 4,4′-oxybis(benzoic) acid (OBA) (0.26 g, 1 mM), imidazole (0.068 g, 1 mM), and KOH (0.11 g, 2 mM) and 8 mL of water was heated in a poly(tetrafluoroethylene) (PTFE)-lined stainless steel autoclave at different times (1−5 days) and temperatures (75−220 °C) under autogenous pressure. The synthesis conditions and other related parameters are summarized in Table 1. The synthesis efforts resulted in a total of six different phases identified by single-crystal X-ray diffraction (XRD). The products of the synthesis were initially characterized by powder XRD studies, which indicated that in some of the preparations mixed-phase products are obtained. In most of the cases, we observed a reasonable yield for the products, which are typically in the range of 70−75% based on Mn.

(b) Synthesis of Mn-1,2,4-BTC Compounds. A typical reaction mixture containing $Mn(OAc)_2 \cdot 4H_2O$ (0.245 g, 1 mM), 1,2,4-benzenetricarboxlic acid (0.21 g, 1 mM), imidazole (0.068 g, 1

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Table 1. Data for the Manganese Oxybis(benzoate) Structures and Manganese Trimellitates

compound	synthesis temperature (°C)/time (h)[a]	H_2O/M^{2+}[b]	density (g cm^{-3})	M^{2+}/COO^-	$M^{2+}/10^3$ Å^3	dimensionality[c]
		Manganese Oxybis(benzoate) Structures				
$KMn_2(OH)(H_2O)_6(OBA)_2$ (**1**)	75/24	3 (2)	1.681	1.25	2.59	3 (2)
$Mn(H_2O)_3(OBA)\cdot H_2O$ (**2**)	110/24	4 (3)	1.578	1.5	2.49	2 (0)
$Mn(H_2O)(OBA)$ (**3**)	150/24	1 (1)	1.664	2	3.04	2 (0)
$Mn(H_2O)_2(OBAH)_2$ (**4**)	150/48	2 (2)	1.572	2	1.56	2 (0)
$Mn(H_2O)(Im)_2(OBA)$ (**5**)	180/72	1 (1)	1.465	1	1.9	1 (0)
$Mn_2(OH)_2(OBA)$ (**6**)	220/24	0 (0)	2.001	3	6.02	3 (2)
		Manganese Trimellitates				
$Mn_2(OH)(H_2O)_2(BTC)\cdot 2H_2O$ (**7**)	110/24	2 (1)	2.096	2.33	6.28	3 (0)
$Mn(H_2O)(BTCH)\cdot H_2O$ (**8**)	180/48	2 (1)	2.017	1.33	4.06	3 (0)
$Mn_3(BTC)_2$ (**9**)	220/24	0 (0)	2.424	2.67	7.56	3 (2)

[a] Based on the first observation of the phase (lowest temperature and smallest reaction time). [b] The first number in the H_2O/Co^{2+} column refers to the total water content, and the second, given in parentheses, refers to coordinated water molecules. [c] The first number in the dimensionality column refers to the total dimensionality and the second to the inorganic dimensionality.

Table 2. Crystal Data and Structure Refinement Parameters for Compounds **1**, **4**, **5**, **7**, and **8** Isolated during the Present Study

	1	**4**	**5**	**7**	**8**
empirical formula	$C_{28}H_{29}O_{17}KMn_2$	$C_{28}H_{22}O_{12}Mn$	$C_{20}H_{18}N_4O_6Mn$	$C_9H_{12}O_{11}Mn_2$	$C_9H_8O_8Mn$
fw	786.46	605.40	465.32	406.03	299.09
cryst syst	orthorhombic	triclinic	triclinic	triclinic	triclinic
space group	*Pbca* (No. 61)	*P*1 (no.1)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a (Å)	11.4256(9)	5.0218(11)	8.496(2)	6.6108(8)	6.3999(14)
b (Å)	17.3545(13)	5.0344(11)	9.581(2)	9.2901(11)	7.3424(15)
c (Å)	31.182(2)	25.438(5)	13.225(3)	11.2290(13)	10.868(2)
α (deg)	90.0	88.593(3)	98.988(4)	111.538(2)	92.197(4)
β (deg)	90.0	88.101(3)	92.752(4)	92.512(2)	100.979(3)
γ (deg)	90.0	84.484(4)	96.294(4)	95.010(2)	100.017(4)
volume (Å^3)	6183.0(8)	639.6(2)	1054.5(4)	3178.0(13)	492.35(18)
Z	8	1	2	2	2
temperature (K)	273(2)	293(2)	293(2)	293(2)	293(2)
ρ_{calcd} (g cm^{-3})	1.681	1.572	1.465	2.096	2.017
μ (mm^{-1})	1.033	0.586	0.670	2.043	1.376
wavelength (Å)	0.710 73	0.710 73	0.710 73	0.710 73	0.710 73
θ range (deg)	2.21−28.02	2.40−28.02	2.17−28.02	1.96−27.99	3.29−27.99
R index [$I > 2\sigma(I)$][a]	R1 = 0.0790, wR2 = 0.1246	R1 = 0.0635, wR2 = 0.1635	R1 = 0.0495, wR2 = 0.1322	R1 = 0.0495, wR2 = 0.1117	R1 = 0.0481, wR2 = 0.0992
R (all data)[a]	R1 = 0.1493, wR2 = 0.1457	R1 = 0.0666, wR2 = 0.1683	R1 = 0.0598, wR2 = 0.1392	R1 = 0.0644, wR2 = 0.1187	R1 = 0.0589, wR2 = 0.1033

[a] $R1 = \|F_o| - |F_c\|/\sum|F_o|$; $wR2 = (\sum[w(F_o^2 - F_c^2)]/\sum[w(F_o^2)^2])^{1/2}$. $w = 1/[\rho^2(F_o)^2 + (aP)^2 + bP]$. $P = [\max(F_o, O) + 2(F_c)^2]/3$, where $a = 0.0447$ and $b = 1.3185$ for **1**, $a = 0.1183$ and $b = 0.6211$ for **4**, $a = 0.0757$ and $b = 0.4166$ for **5**, $a = 0.0483$ and $b = 1.6860$ for **7**, and $a = 0.0236$ and $b = 1.6728$ for **8**.

mM), and KOH (0.11 g, 1 mM) and 8 mL of water was heated in a PTFE-lined stainless steel autoclave at different times (1−5 days) and temperatures (75−220 °C) under autogenous pressure. The synthesis conditions and other related parameters are summarized in Table 1. We have not been able to isolate any insoluble solid-phase products from the reaction mixture when the reactions were carried out at 75 °C, which always resulted in a clear solution. The synthesis efforts at other temperatures resulted in a total of three different phases identified by single-crystal XRD. The products were characterized by powder XRD studies, which indicated a mixture of products in some of the preparations. In most of the cases, we observed a reasonable yield for the products, which are typically in the range of 65−70% based on Mn.

Single-Crystal Structure Determination. A suitable single crystal of each compound was carefully selected under a polarizing microscope and glued carefully to a thin glass fiber. The single-crystal data were collected on a Bruker AXS SMART Apex CCD diffractometer at 293(2) K. The X-ray generator was operated at 50 kV and 35 mA using Mo Kα ($\lambda = 0.710\ 73$ Å) radiation. Data were collected with a ω scan width of 0.3°. A total of 606 frames were collected in three different settings of φ (0, 90, and 180°), keeping the sample-to-detector distance fixed at 6.03 cm and the detector position (2θ) fixed at −25°. The data were reduced using *SAINTPLUS*,[16] and an empirical absorption correction was applied using the *SADABS* program.[17] The structure was solved by *SHELXS97*[18] and refined using *SHELXL97*[18] present in the *WinGx* suit of programs (version 1.63.04a).[19] Final refinement included atomic positions for all of the atoms, anisotropic thermal parameters for all of the non-hydrogen atoms, and isotropic thermal parameters for all of the hydrogen atoms. Full-matrix least-squares refinement against F^2 was carried out using the *WinGx* package of programs.[19] Details of the structure solution and final refinements for the new compounds identified in the present investigation, $KMn_2(OH)(H_2O)_6(OBA)_2$ (**1**), $Mn(H_2O)_2(OBAH)_2$ (**4**), $Mn(H_2O)(Im)_2(OBA)$ (**5**), $Mn_2(OH)(H_2O)_2(BTC)\cdot 2H_2O$ (**7**), and $Mn(H_2O)(BTCH)\cdot H_2O$ (**8**), are given in Table 2. CCDC 683492 (**1**), 683493 (**4**), 683494 (**5**), 678766 (**7**), and 683495 (**8**) contain the crystallographic data for this paper. The numbers for the other compounds are CCDC 648374 [$Mn(H_2O)_3(OBA)\cdot H_2O$ (**2**)], 648375 [$Mn(H_2O)(OBA)$ (**3**)],

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637649 [$Mn_2(OH)_2(OBA)$ (**6**)], and 637648 [$Mn_3(BTC)_2$ (**9**)]. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre (CCDC) via www.ccdc.cam.ac.uk/data_request/cif.

Results

Here we briefly describe the results of the earlier studies on three different systems of compounds as a function of the variation in the reaction temperature.

(a) Cobalt Succinate Phases. Cobalt succinates is the first system of compounds investigated to study the effect of temperature because they represent a well-established family of compounds.[10,20] Cheetham and co-workers carried out a systematic study of the role of temperature in the formation of the various cobalt succinate phases by keeping the same reaction mixture.[10] During the study, five cobalt succinate phases were identified when cobalt(II) hydroxide was reacted with succinic acid in a 1:1 molar ratio at five different temperature in the range of 60−250 °C (Figure 1). This study, the first of its kind, clearly showed the formation of one-dimensional structures with hydrated metal centers up to 100 °C, two-dimensional structures with hydrated metal centers at 150 °C, and three-dimensional structures possessing −M−O−M− connectivities at higher temperatures (Table 3). The notable outcome of the study is that the water coordinating with the cobalt atoms in the structures continuously decreases with increasing temperature, suggesting an increased entropy contribution. In addition, the loss of water molecules from the coordination sphere of the cobalt atoms forces the nearby cobalt atoms to come closer and form the −M−O−M− linkages, thereby increasing the total density of the system. This study paved the way for the investigation of other variables such as the reaction time, which would probe the role of thermodynamic and kinetic factors in the formation of extended MOF structures.

In a subsequent paper, Cheetham and co-workers using a high-throughput investigation studied the role of the pH, temperature, concentration, and time of synthesis of the cobalt succinate MOFs.[10b] This study revealed the presence of two new phases in addition to the five compounds isolated during their study on the role of temperature.[10a] From this, it appears that there is competition between the many closely related phases and the reaction mixture is under a constant change of equilibrium at any given period of time and temperature. Additionally, the study also reveals the importance and subtle relationship needed between the temperature, acid/base ratio (concentration) and time in determining the favorable structure.

(b) Cobalt Pyridine-3,4-dicarboxylate Phases. Kitagawa and co-workers investigated the effect of both the time and temperature on the formation of cobalt pyridine-3,4-dicarboxylate phases.[12] In this study, $CoCl_2 \cdot 6H_2O$, pyridine-3,4-dicarboxylic acid, NaOH, and water in the ratio 1:1:2:555 were heated at 150 °C/24 h followed by at 180 °C/24 h (Table 3). Similar to the behavior observed with the cobalt succinate phases,[10] a two-dimensional compound possessing water-coordinated octahedral cobalt centers was isolated at 150 °C and a three-dimensional compound with one-dimensional −M−O−M− linkages was obtained at 180 °C (Figure 2). This study suggests that it is likely that the two-dimensional phase could have transformed into the three-dimensional compound because the reaction mixture yielded only the two-dimensional compound at 150 °C. Though the result of this study appears to be similar to that observed by Cheetham and co-workers,[10] it does not indicate the possible role of time in the formation of the different phases. This study also shows the formation of −Co−O−Co− linkages at higher temperatures accompanied by a decrease in the coordinated water molecules bound to the central cobalt atom.

(c) Cadmium Camphorate Phases. Recently, Bu and co-workers reported the role of temperature and the composition of the reaction mixture in the formation of a family of homochiral cadmium camphorates (Table 3 and Figure 3).[13] In this study, 6 mL of ethanol was layered onto a mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (0.0815 g), Na_2CO_3 (0.0253 g), D-camphoric acid (0.0512 g), and 2 mL of water at room temperature. Slow diffusion over several days yielded a hydrated three-dimensional compound with one-dimensional −M−O−M− linkages. When a mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (0.1546 g), Na_2CO_3 (0.0528 g), D-camphoric acid (0.1075), 2 g of water, and 6.1 g of ethanol were heated at 140 °C/3 days, a three-dimensional structure with fewer water molecules was isolated. An anhydrous three-dimensional structure was isolated when a mixture of $Cd(NO_3)_2 \cdot 4H_2O$ (0.1507 g), Na_2CO_3 (0.0530 g), D-camphoric acid (0.1004 g), 2.4 g of water, and 4.44 g of ethylene glycol was heated at 180 °C/5 days. In this study, the composition was varied along with the temperature in obtaining the products. The total water content of the different products obtained decreases with increasing reaction temperature, similar to those observed by Cheetham and co-workers[10] and Kitagawa and co-workers.[12]

(d) Manganese Oxybis(benzoate) Phases. As mentioned earlier, we have been interested in the study of the effect of temperature on a particular composition during the synthesis of MOF compounds.[15] During this study, we have investigated the formation of manganese oxybis(benzoate) phases by reacting a mixture of $Mn(OAc)_2 \cdot 4H_2O$ (0.245 g, 1 mM), 4,4′-oxybis(benzoic acid) (0.26 g, 1 mM), imidazole (0.068 g, 1 mM), and NaOH (0.08 g, 2 mM) and 8 mL of water in a 23 mL autoclave in the temperature range of 80−220 °C for 24 h. The reaction yielded three distinct phases with two- and three-dimensional structures. Similar to the earlier observations,[10] the water molecules were found to be coordinated with the metal center at low temperatures and at high temperatures, the three-dimensional structures possessed two-dimensional −M−O−M− linkages. The three-dimensional structure has a brucite-related two-dimensional lattice, which was observed for the first time.

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[20] (a) Livage, C.; Egger, C.; Ferey, G. *Chem. Mater.* **2001**, *13*, 410. (b) Livage, C.; Egger, C.; Ferey, G. *Chem. Mater.* **1999**, *11*, 1546. (c) Long, L. S.; Chen, X. M.; Tong, M. L.; Sun, Z. G.; Ren, Y. P.; Huang, R. B.; Zheng, L. S. *J. Chem. Soc., Dalton Trans.* **2001**, 2888. (d) Livage, C.; Egger, C.; Nogues, M.; Ferey, G. *J. Mater. Chem.* **1998**, *8*, 2743.

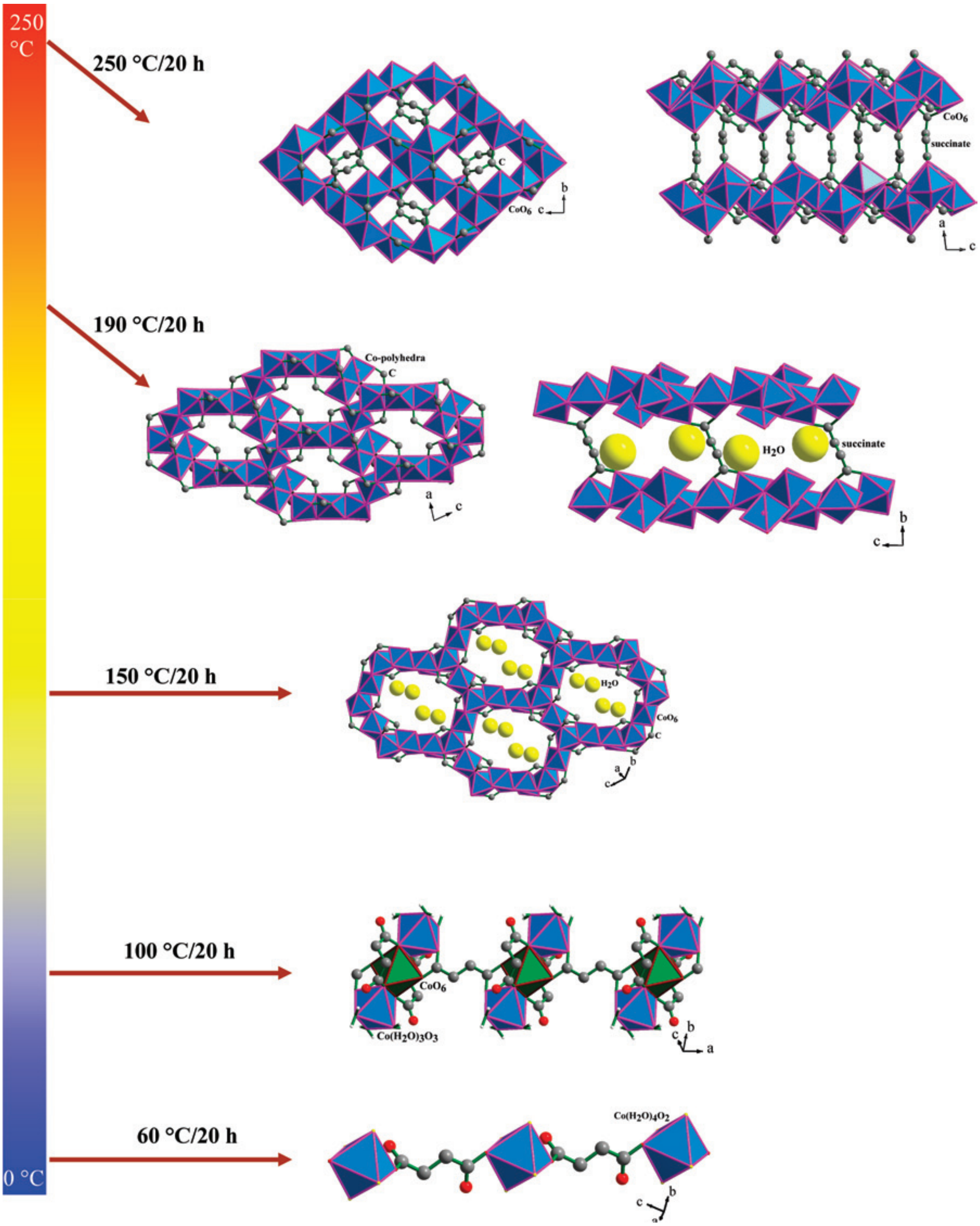

Figure 1. Structures of the five cobalt succinate phases: $Co(H_2O)_4(C_4H_4O_4)$, $Co(H_2O)_2(C_4H_4O_4)$, $Co_4(H_2O)_2(OH)_2(C_4H_4O_4)_3 \cdot 2H_2O$, $Co_6(OH)_2(C_4H_4O_4)_5 \cdot H_2O$, and $Co_5(OH)_2(C_4H_4O_4)_4$ (from bottom to top). The left-side vertical bar indicates the approximate temperature scale. and the time indicates the first observation of the phase.

Though three distinct structures have been isolated at three different temperatures, it is likely that there may be other related phases because an unidentified phase was observed at low temperatures (80 °C; Figure S4 in the Supporting Information). This suggests that other parameters such as the duration of the reaction (time of reaction) may be of some importance. To test this hypothesis and to validate the argument that the time of reaction can also play a significant role in determining the kinetic versus thermodynamic control in the formation of MOFs,[10] a new set of experiments were carried out. Thus, we employed a reaction composition identical with that employed to study the effect of temperature[15] but performed the reaction using KOH as the base instead of NaOH at varying time intervals (typically 1−5 days) at each temperature. It was observed from our related studies that the use of KOH in the reaction mixture gives rise to good quality single crystals.[21] Because we do not expect to form single-phase solid products in all of our

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(21) Mahata, P.; Sen, D.; Natarajan, S. *Chem. Commun.* **2008**, 1278.

Table 3. Data for the Cobalt Succinates, Cobalt Pyridine-3,4-dicarboxylates, and Cadmium Camphorates

compound	synthesis temperature (°C)/time (h)	H_2O/M^{2+a}	density (g cm^{-3})	M^{2+}/COO^-	$M^{2+}/10^3$ Å^3	dimensionality^b
Cobalt Succinates						
$Co(H_2O)_4(C_4H_4O_4)$	60/20	4 (4)	1.945	1	4.74	1 (0)
$Co(H_2O)_2(C_4H_4O_4)$	100/20	2 (2)	1.926	2	5.50	1 (0)
$Co_4(H_2O)_2(OH)_2(C_4H_4O_4)_3\cdot 2H_2O$	150/20	1 ($^1/_2$)	2.085	2.67	7.28	2 (2)
$Co_6(OH)_2(C_4H_4O_4)_5\cdot H_2O$	190/20	$^1/_6$ (0)	2.197	2.8	8.05	3 (2)
$Co_5(OH)_2(C_4H_4O_4)_4$	250/20	0 (0)	2.337	3	8.88	3 (2)
Cobalt Pyridine-3,4-dicarboxylates						
$Co(H_2O)_2(C_3H_3NO_4)\cdot H_2O$	150/24	3 (2)	2.038	1.5	4.44	2 (0)
$Co_3(OH)_2(C_3H_3NO_4)_2(H_2O)_2$	150/24 + 180/24	$^2/_3$ ($^2/_3$)	2.361	2	7.39	3 (1)
Cadmium Camphorates						
$Cd_2(H_2O)_3(C_{10}H_{14}O_4)_2$	RT/several days	$^3/_2$ ($^3/_2$)	1.557	2	2.78	3 (1)
$Cd_4(H_2O)(C_{10}H_{14}O_4)_4\cdot H_2O$	140/72	$^1/_2$ ($^1/_4$)	1.901	2.25	3.58	3 (1)
$Cd_2(C_{10}H_{14}O_4)_2$	180/120	0 (0)	1.948	2	3.78	3 (1)

[a] The first number in the H_2O/Co^{2+} column refers to the total water content, and the second, given in parentheses, refers to the coordinated water molecules. [b] The first number in the dimensionality column refers to the total dimensionality and the second to the inorganic dimensionality.

reactions, it would be desirable to have a mixture of single-crystalline products rather than a mixture of powder samples because the structural characterization can be made by using the single-crystal XRD. This prompted us to study the effect of time and temperature by using KOH as the secondary base in all of our reactions. The resulting product of each experiment was analyzed using powder XRD studies, and the results are presented as a two-dimensional temperature vs time plot in Figure 4 (for the experimental powder XRD patterns, see Figure S6−S10 in the Supporting Information).

The time dependence study revealed the presence of three new additional phases, making a grand total of six phases in the manganese oxybis(benzoate) family of compounds (Figure 5). Here we describe briefly the structures of the new compounds isolated in the present study.

Compound **I** was obtained as a pure single-phase material during the reaction at 75 °C/24 h. The simulated powder XRD pattern of this phase matched with the previously unknown phase obtained using NaOH as a base at 80 °C. Compound **1** has a three-dimensional structure with K^+ ions as part of the framework. The asymmetric unit of **I** consists of two crystallographically independent octahedral Mn^{2+} ions, one K^+ ion, two 4,4′-oxybis(benzoate) (OBA) anions, one μ_3-OH, and six coordinated water molecules. Thus, Mn(1) is coordinated by two carboxylate oxygen atoms, three H_2O molecules (two of them have μ_2-connectivity), and one μ_3-OH group, and Mn(2) is coordinated by three carboxylate oxygen atoms, one water molecule, and two μ_3-OH groups. The K^+ ion is five-coordinated with one carboxylate oxygen atom and four water molecules (two of them have μ_2-connectivity). The structure contains a rhombus-shaped tetranuclear cluster of the formula $[Mn_4(\mu_3\text{-}OH)_2(H_2O)_8O_{10}]$, formed by the two Mn atoms, Mn(1) and Mn(2), which are related by the center of symmetry. A −OH group [O(1)] has a μ_3-connectivity linking Mn(1), Mn(2), and Mn(2a). The Mn_4 clusters are connected by $K(H_2O)_4O$ polyhedra, forming two-dimensional mixed-metal layers, which are connected by the OBA units, completing the three-dimensional structure.

Compound **2** has a pseudo-two-dimensional structure, and **3** has a two-dimensional structure.[15] Compound **4** was isolated from a reaction that produced multiple phases by heating the reaction mixture at 150 °C for 48 h. The single-crystal structure reveals that it also has a two-dimensional structure but with free carboxylic acid groups. The asymmetric unit has one crystallography independent Mn^{2+} ion, two OBAH anions [monoanionic 4,4′-oxybis(benzoic acid)], and two coordinated water molecules. The octahedral Mn^{2+} ions are coordinated by four carboxylate oxygen atoms and two water molecules. The connectivity between Mn^{2+} ions and the carboxylate groups forms a two-dimensional layer. The short O−O contact distances (2.62 and 2.66 Å) between the free carboxylic acid groups of the two adjacent layers suggest that the layers are strongly hydrogen bonded with each other.

Compound **5** was also formed as a mixture of phases by heating the reaction mixture at 180 °C for 72 h. The single-crystal X-ray structure studies reveal a one-dimensional structure. The asymmetric unit of **5** has one crystallographically independent Mn^{2+} ion, one OBA anion, two imidazole molecules, and one coordinated water molecule. The octahedral Mn^{2+} ions are coordinated by three carboxylate oxygen atoms, two nitrogen atoms of two different imidazole molecules, and one coordinated water molecule. The connectivity between the Mn^{2+} ion and OBA forms a simple one-dimensional structure with the bound imidazole molecules hanging as a pendent in the interchain region. The structure is stabilized by many different weak interactions, which include the hydrogen-bonding ($O-H\cdots O$, $C-H\cdots O$, and $N-H\cdots O$) and $N-H\cdots\pi$ interactions. Compound **6** has a three-dimensional structure with two-dimensional −M−O−M− connected layers that closely resemble those observed in brucite and related structures.[15]

The powder XRD patterns of each preparation were compared with the simulated XRD patterns of each compound (**1**−**6**), generated from the single-crystal X-ray structures, which indicated few interesting observations. Thus, the previously unidentified phase formed at low temperature (T < 100 °C) during our studies on the effect of temperature[15] was found to correlate with the simulated XRD pattern of the K^+ phase, compound **1**. It may be noted that we were unable to obtain a suitable single crystal when NaOH was used in the reaction mixture, which precluded this identification.[15] From Figure 4, it becomes apparent that

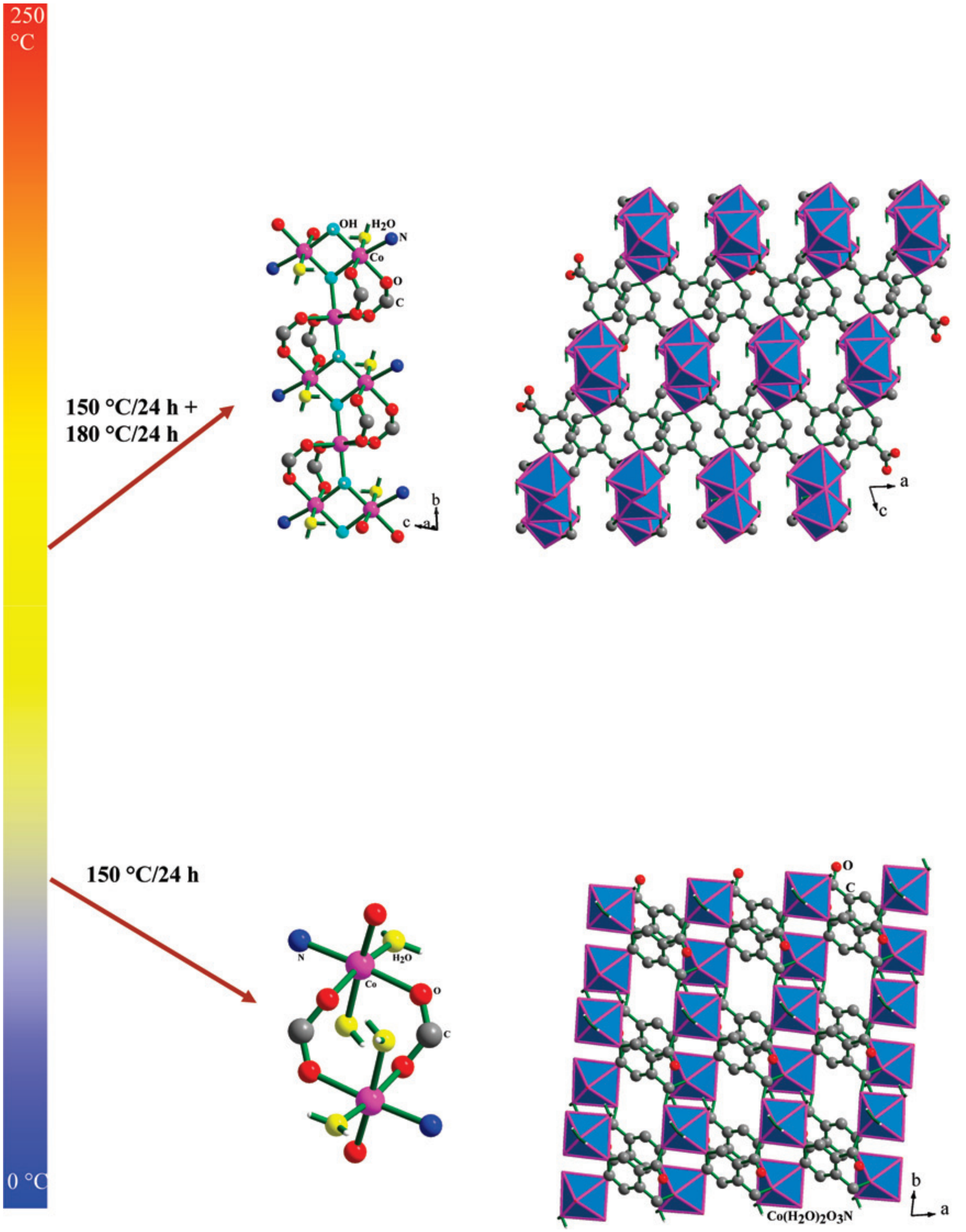

Figure 2. Structures of two the cobalt pyridine-3,4-dicarboxylate phases: Co(H$_2$O)$_2$(C$_3$H$_3$NO$_4$).H$_2$O (bottom) and Co$_3$(OH)$_2$(C$_3$H$_3$NO$_4$)$_2$(H$_2$O)$_2$ (top). The left-side bar indicates the approximate temperature scale.

this phase persists up to 4 days at low temperatures and vanishes at higher temperatures irrespective of the duration of the reaction. The formation of Mn^{2+} clusters at low temperatures has been known.[22] Thus, it is not totally unexpected to observe the presence of Mn$_4$ cluster units in the present study. Interestingly, when the reaction mixture was heated for a longer duration, two more new compounds, **4** and **5** with two- and one-dimensional structures, have been isolated. Of these, **4** appears to be more stable compared to the imidazole-bound structure (**5**), which forms only when the reaction mixture was heated at 180 °C for 3 days. In all of the cases, irrespective of the time of the reaction, the highest temperature phase always corresponds to the brucite-related structure, compound **6**, having two-dimensional −M−O−M− linkages. The time of the reaction definitely has a bearing on the formation of **6** because we observe this phase at 180 °C after heating for 5 days (Figure 4e). From the present study, it becomes clear that the total water in the structures, whether coordinated or free water, continuously decreases with increasing temperature and time. Less water at higher temperatures (T > 180 °C) is likely driven by the increased entropic contribution associated with the release

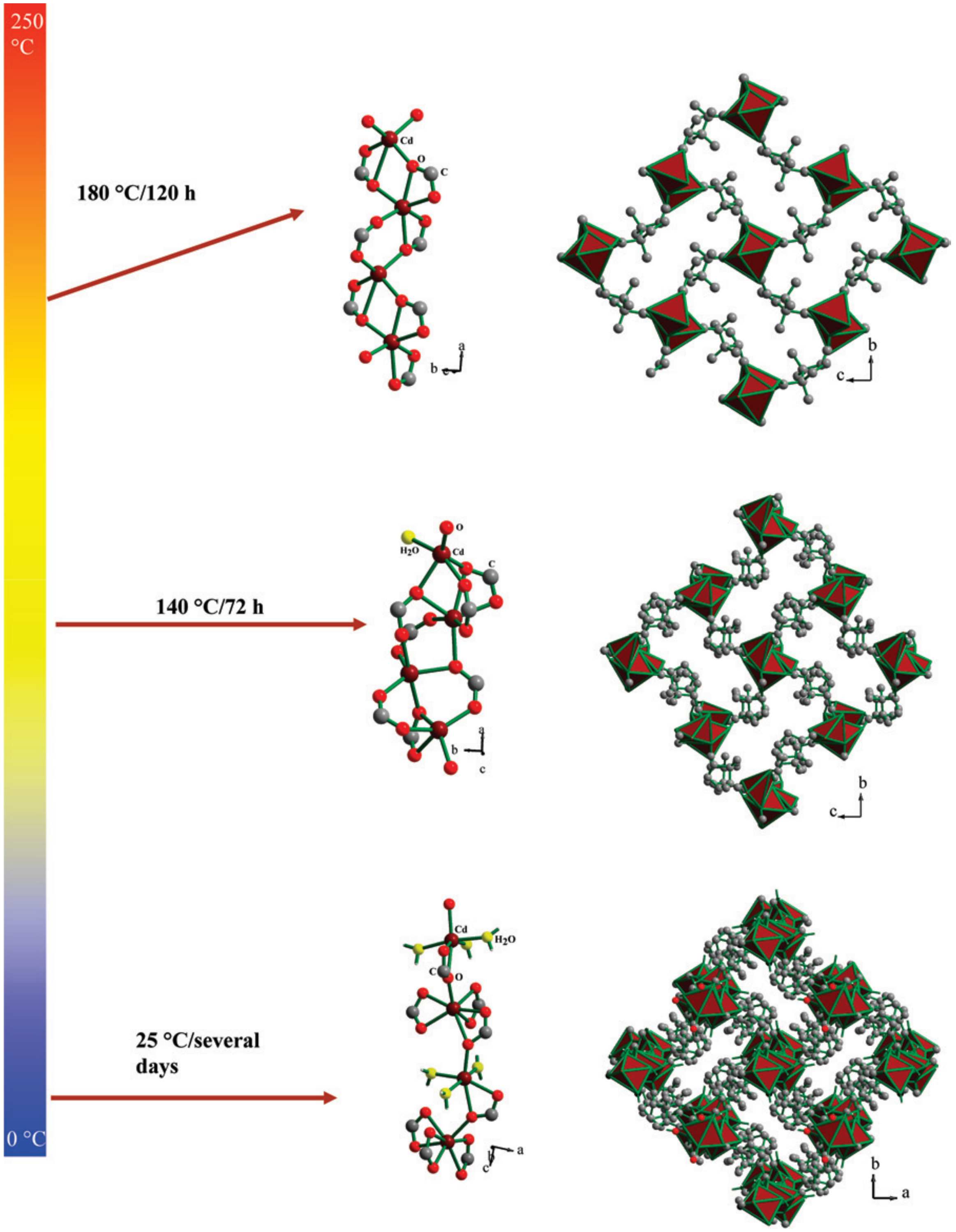

Figure 3. Structures of the three cadmium camphorate phases: $Cd_2(H_2O)_3(C_{10}H_{14}O_4)_2$, $Cd_4(H_2O)(C_{10}H_{14}O_4)_4 \cdot H_2O$, and $Cd_2(C_{10}H_{14}O_4)_2$ (from bottom to top). The left-side bar indicates the approximate temperature scale.

of water. The present observations show that there are subtle relationships that exist between the temperature and time of reaction, which indirectly influences the formation of more stable compounds of higher dimensionality with −M−O−M− linkages. In addition, the decreasing dielectric constant of water at high temperature under hydrothermal conditions may also favor higher coordination numbers for the carboxylate oxygen atoms as well.

(e) Manganese Trimellitate (Benzene-1,2,4-tricarboxylate) Phases. Similar to the manganese oxybis(benzoate) structures, we have carried out investigations on the role of time and temperature in the formation of manganese trimellitate phases. Thus, a reaction mixture of $Mn(OAc)_2 \cdot 4H_2O$ (0.245 g, 1 mM), trimellitic acid (0.21 g, 1 mM), imidazole (0.068 g, 1 mM), and KOH (0.11 g, 2 mM) and 8 mL of water was heated in a 23 mL autoclave in the temperature

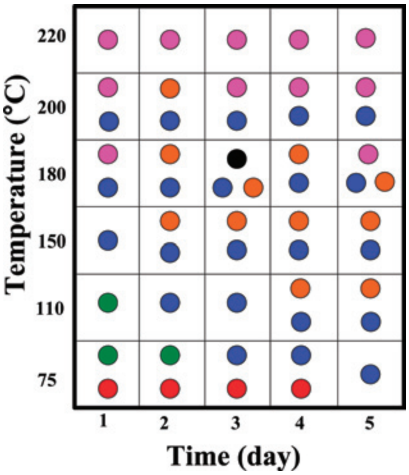

Figure 4. Temperature vs time plot of the various manganese oxybis(benzoate) phases isolated and identified using powder XRD patterns. The various phases were identified by comparing the powder XRD pattern with the simulated pattern generated from the single-crystal structure. Color code: **1**, red; **2**, green; **3**, blue; **4**, orange; **5**, black; **6**, pink.

range of 75−220 °C for varying durations (1−5 days). The resulting product of each experiment was subjected to powder XRD studies, and the results are presented as a two-dimensional temperature vs time plot in Figure 6 (for the experimental powder XRD patterns, see Figures S11−S15 in the Supporting Information). During the study of this system, we did not observe any water-insoluble crystalline products at lower temperatures ($T < 100$ °C). The higher temperature reactions yielded three distinct crystalline compounds with three-dimensional structures, **7**−**9** (Figure 7). Similar to the earlier observations, water molecules were found to be coordinated with the metal center at lower temperatures, and at higher temperature, the three-dimensional structure has two-dimensional −M−O−M− linkages. The compound formed at 220 °C, **9**, has a distorted Kagome-related two-dimensional lattice, which is the only example of a single-atom-bridged −M−O−M− Kagome layer in MOFs.[21] Of the three different compounds, identified and isolated during the present study, compound **9** has been described recently by us[21] and the other two structures (**7** and **8**) would be presented briefly here.

Compound **7** has been obtained as a pure single-phase material when the reaction mixture was heated at 110 °C for 24 h. The structure determined by single-crystal XRD studies indicates a three-dimensional network with one-dimensional water-filled channels. The asymmetric unit of **7** consists of two crystallographically independent Mn^{2+} ions, one trimellitate anion, one μ_3-OH, and two coordinated and two extraframework water molecules. The structure contains a rhombus-shaped tetranuclear cluster of the formula $[Mn_4(\mu_3\text{-}OH)_2(H_2O)_4O_{12}]$, formed by the two octahedrally coordinated Mn atoms, Mn(1) and Mn(2), which are related by the center of symmetry. A −OH group [O(2)] has a μ_3-connectivity linking Mn(1), Mn(2), and Mn(2a) and a μ_3-carboxylate oxygen [O(6)] connecting Mn(1) and Mn(2). The Mn_4 clusters are connected by trimelliate anions, forming a three-dimensional structure with one-dimensional channels occupied by two extraframework water molecules [O(100) and O(200)]. This structure is closely related to the structure of **1** obtained by the reaction of Mn^{2+} and OBA in the presence of KOH.

Compound **8** was formed as a mixture of phases (**7** and **8**) by heating the reaction mixture at 180 °C for 48 h. The single-crystal XRD studies reveal a three-dimensional structure with one-dimensional water-filled channels. The asymmetric unit of this compound consists of one crystallographically independent Mn^{2+} ion, one dianionic trimelliate anion, and one coordinated and one extraframework water molecules. The Mn^{2+} ion is bound with four carboxylate oxygen atoms and two μ_2-H_2O molecules. The μ_2-H_2O molecules connect the Mn centers to form a dimer of the formula $[Mn_2(\mu_2\text{-}H_2O)_2O_8]$, which are linked through the bidentate carboxylate groups, giving rise to a one-dimensional structure, which are further connected by trimelliate anions, forming the three-dimensional structure with one-dimensional channels occupied by the extraframework water molecules.

A careful study of the powder XRD patterns of the products of the reaction between Mn^{2+} and trimellitic acid and a comparison with the simulated XRD patterns, generated from the single-crystal XRD structures, reveal few generalities (Figure 6). The notable observation is that there is no solid-phase product for the reaction carried out at low temperatures ($T < 100$ °C) irrespective of the time of the reaction (1−5 days). The Mn_4 cluster compound (**7**), which forms initially at 110 °C, appears to be stable up to 200 °C. Interestingly, the related structure, the Mn_2 dimer compound **8**, starts to form around 180 °C when the reaction mixture was heated for 2 days and appears to be stable up to 200 °C. This indicates a very narrow range of stability for this phase (∼20 °C). Similar to the observation in the oxybis(benzoate) structures, the formation of Kagome-related −M−O−M− linked layers has some dependence on the time of reaction. The formation of compound **9** was observed at 180 °C after 3 days (Figure 6), while it forms only at 220 °C when heated for 24 h (Figure 6). This indicates that compound **9** may be the kinetically stable phase at higher temperatures (220 °C/24 h), while it could be the thermodynamically stable phase because the formation was observed at lower temperature (180 °C) when the reactions were carried for a longer duration (>3 days). This observation is consistent with other similar observations in the literature,[10,13] indicating a trend in the formation of the MOFs where a subtle balance between the kinetic and thermodynamic factors would be required to isolate the preferred phase. In addition, the total water content of the system also decreases continuously when the reaction temperature is increased, indicating a reasonable entropy-driven control.

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(22) (a) Piligkos, S.; Rajaraman, G.; Soler, M.; Kirchner, N.; Slageren, J. V.; Birchen, R.; Parsons, S.; Gudel, H. U.; Kortus, J.; Wernsdorfer, W.; Christou, G.; Brechin, E. K. *J. Am. Chem. Soc.* **2005**, *127*, 5572. (b) Tasiopoulos, A. J.; Vinslava, A.; Wernsdorfer, W.; Abboud, K. A.; Christou, G. *Angew. Chem., Int. Ed.* **2004**, *43*, 2117. (c) Ruiz, D.; Sun, Z.; Albela, B.; Folting, K.; Ribas, J.; Christou, G.; Hendrickson, D. N. *Angew. Chem., Int. Ed.* **1998**, *37*, 300.

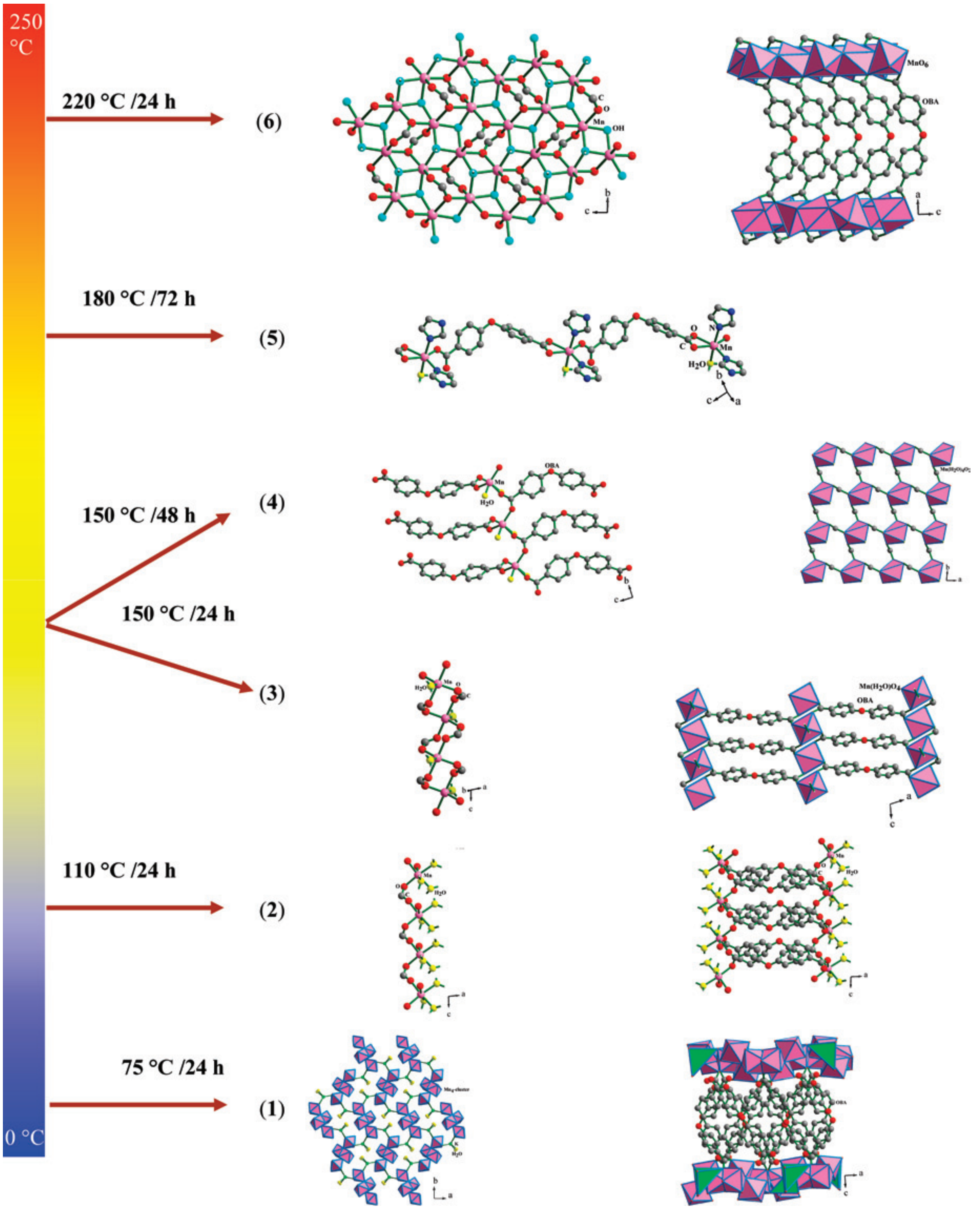

Figure 5. Structures of the six manganese oxybis(benzoate) phases: $KMn_2(OH)(H_2O)_6(OBA)_2$ (**1**), $Mn(H_2O)_3(OBA)\cdot H_2O$ (**2**), $Mn(H_2O)(OBA)$ (**3**), $Mn(H_2O)_2(OBAH)_2$ (**4**), $Mn(H_2O)(Im)_2(OBA)$ (**5**), and $Mn_2(OH)_2(OBA)$ (**6**) (from bottom to top). The left-side bar indicates the approximate temperature scale, and the time indicates the first observation of the phase.

Discussion

The above results on manganese oxybis(benzoate) and trimellitate compounds can be compared with other similar studies available in the literature.[10,12,13,15] In the manganese oxybis(benzoate) system of compounds, a systematic increase with respect to density, M^{2+}/COO^-, and the number of M^{2+} ions per 1000 Å as a function of the temperature can be observed (Table 1 and Figure 4). This observation is similar to that of the cobalt succinate phases reported earlier (Table 3).[10] We have also estimated the above parameters for the cobalt pyridinedicarboxylate[12] and the cadmium camphorate phases,[13] which also show similar behavior. In addition, there is an overall dimensionality increase in all of the cases. It is likely that these changes are a consequence of the changing coordination around the central metal ions and represent trends that are common to the five systems of compounds described here.

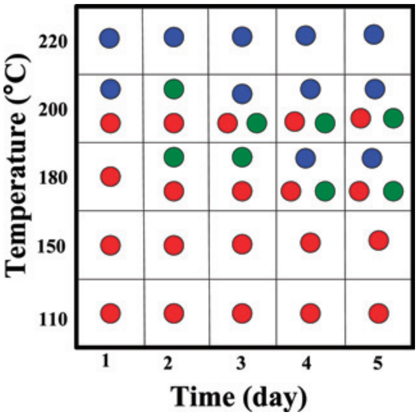

Figure 6. Temperature vs time plot of the various manganese trimellitate phases isolated and identified using powder XRD patterns. The various phases were identified by comparing the powder XRD pattern with the simulated pattern generated from the single-crystal structure. Color code: **7**, red; **8**, green; **9**, blue.

During the present study, we have also made efforts to identify the role of the time of reaction in the formation of hybrid compounds. The earlier study by Cheetham and co-workers using a high-throughput investigation on the cobalt succinates revealed the formation of two new phases[8b] in addition to the five phases identified earlier.[10] From the results of the present study (Table 1), it becomes clear that the role of the time of reaction does not follow any simple systematic behavior. From Table 1, the number of metal ions per carboxylate appears to show a continuous increase as a function of the time and temperature; with the only anomaly being the one-dimensional compound with bound imidazole, compound **5**. It has been postulated that at higher temperature there is a competition between the water molecules that may be bound to the metal and the carboxylate present in solution, leading to the formation of a higher dimensional structure with −M−O−M− connectivity.[10,15] In addition, it is known that most of these compounds are formed by a mechanism involving dissolution and recrystallization,[23] which implies that there is a continuous change in the equilibrium in solution. During the present study, the loss of the carboxylate unit paved the way for the imidazole molecules to bind with the metal center, giving rise to this rather unusual, but not totally unexpected, one-dimensional coordination polymer that may be reactive. To this end, it may be noted that, during the study on zinc phosphate based open-framework structures, it has been postulated that the one-dimensional structures could be precursors for the structure of higher dimensionality.[24]

The formation of a Mn_4 cluster compound, compounds **1** and **7**, at $T \sim 100$ °C with three-dimensional connectivity is also intriguing. One way of rationalizing this is by considering other known manganese cluster compounds in the literature, which are typically prepared at $T < 100$ °C,[22] and it may be expected that such clusters could form in our preparations. Similar clustering of metal ions has also been observed during the synthesis of cadmium camphorate phases at low temperatures.[13] In addition, we also observe the formation of another three-dimensional phase, compound **8**, which is formed as a mixture and appears to be in equilibrium with compounds **7** and **9**. One way to rationalize the formation of these intermediate phases would be to consider the distribution of charges within the structure, especially at the metal site. This approach has been employed gainfully earlier.[13]

To estimate the charge distribution, we have followed the model employed earlier[13] by considering the coordination environment around each Mn site. In compound **I**, Mn(1) is surrounded by one triply coordinated (with two different Mn^{2+} ions and one K^+ ion) and one bidentate (with two different Mn^{2+} ions) carboxylate groups, one μ^3-OH group, two μ^2-H_2O molecules, and one terminal H_2O molecule, so the charge at this site is thus $[(-1 \times {}^1/_3) + (-1 \times {}^1/_2)]_{COO^-} + [-1 \times {}^1/_3]_{OH^-} + [2]_{Cd} = {}^5/_6$. The Mn(2) atom is surrounded by one monodentate, one bidentate (with two different Mn^{2+} ions), and one triply coordinated (with two different Mn^{2+} ions and one K^+ ion) carboxylate groups, two μ_3-OH groups, and one terminal water molecule. Therefore, the charge at this site is ${}^1/_2-$. The K atom is surrounded by one triply coordinated carboxylate group (with two Mn^{2+} ions and one K^+ ion), two μ_2-H_2O water molecules, and two terminal water molecules. So, the charge of the K site is ${}^2/_3$. The total charge on the two Mn atoms and the one K atom is 1+, which is compensated for by the presence of the free COO^- of the OBA unit. Similar calculations can be performed on the compounds **2**−**6**, which reveals that the charge on the Mn site is zero (all of the five compounds have only one crystallographically independent Mn^{2+} ion). Out of the five compounds, compounds **2**−**5** have a ratio of Mn and COO^- of 1:2, which suggests that the transformation from one structure to the other may not alter the charge on the Mn site. Thus, the structural changes can be brought about by the replacement of a few neutral ligand molecules such as H_2O and imidazole or by a change in the coordination number/mode of the carboxylate group. The change in the coordination number/mode of the carboxylate groups has been observed earlier in obtaining related cobalt succinate structures.[10] This type of rationalizing permits the presence of the intermediate phases at moderate temperature as well as the presence of a mixture of phases, when the total charges at the Mn site are similar, as has been the case for the four structures (**2**−**5**) isolated during the study. In addition, this also indicates that the phases may have comparable energy. Compound **6** also has a charge of zero at the Mn site with a ratio of Mn:COO^- = 1:1, which requires the presence of an OH^- group attached to the Mn site to maintain charge equilibrium. This situation gives rise to a −Mn−(OH)−Mn−(OH)−Mn− type of linkage that resembles the layers commonly encountered in layered double hydroxides.

The charge distribution calculations on the three manganese trimellitate phases, **7**−**9**, reveal that the compounds **7** and **8** have zero charge at the Mn site whereas **9** has two different charges, Mn(1) = ${}^1/_{12}$ and Mn(2) = ${}^1/_6-$. Because

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(24) Choudhury, A.; Neeraj, S.; Natarajan, S.; Rao, C. N. R. *J. Mater. Chem.* **2001**, *11*, 1537.

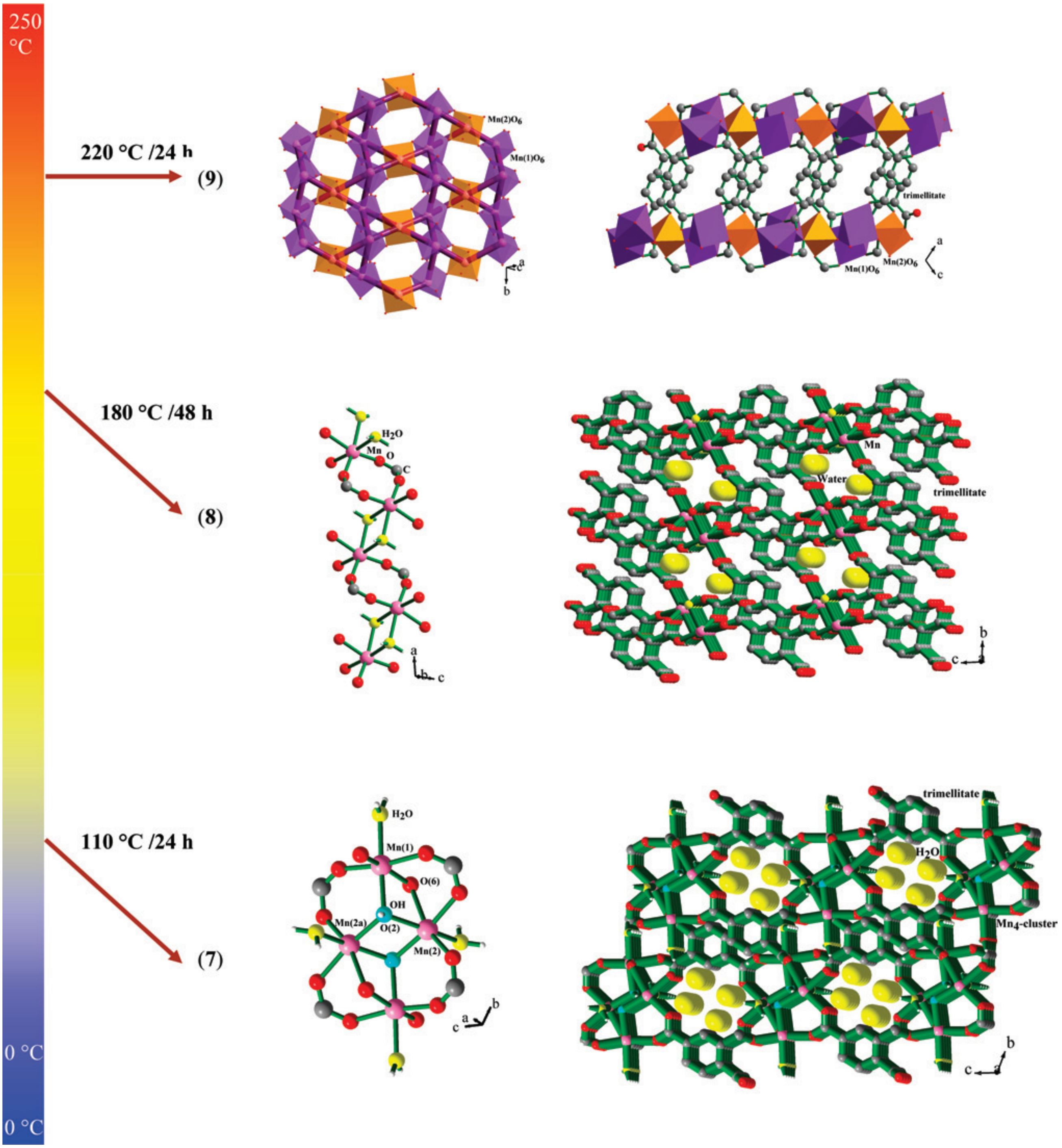

Figure 7. Structures of the three manganese trimelliate phases: $Mn_2(OH)(H_2O)_2(BTC).2H_2O$ (**1**), $Mn(H_2O)(BTCH).H_2O$ (**2**) and $Mn_3(BTC)_2$ (**3**) (from bottom to top). The left-side bar indicates the approximate temperature scale, and the time indicates the first observation of the phase.

the trimellitate anion is triply charged, one would expect different ratios between the Mn and the carboxylate ligand. In **7**, the distribution of the charges at the two Mn sites is being compensated for by the presence of one trimellitate unit and a −OH group. In **8**, the charge at the Mn site is compensated for by the presence of a dianionic trimelliate unit. In **9**, the two differently charged Mn sites are fully compensated for by the presence of one trianionic trimellitate unit. The similar charge distribution along with a comparable ratio of Mn and carboxylate suggests that compound **8** could be an intermediate phase, which may be structurally closer to compound **7**. This is the observed behavior as compound **8** was isolated during the time-dependent study and also observed within a narrow temperature range (∼20 °C).

Conclusions

The dependence of simple variables such as the reaction time and temperature under hydrothermal conditions has been investigated during the preparation of manganese oxybis(benzoate) and manganese trimelliate phases. The studies show that denser three-dimensional structures with infinite −M−O−M− layers are formed at high temperatures irrespective of the duration of the reaction. The appearance of low-dimensional structures at reasonably high temperatures (∼180 °C) and a longer duration (∼3 days) indicates a subtle balance between the local coordination environment of manganese, the available carboxylate units, the water molecules, and the secondary base. This shows a possible kinetic role in the formation of such structures, which is also suggested by the charge distribution calculations at the Mn site. The results of the present study appear to favor overwhelmingly thermodynamic control, and many more such investigations would be required to arrive at a more meaningful correlation and also to establish the close and subtle relationships between thermodynamic and kinetic control in the formation of MOF compounds.

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Supporting Information Available: X-ray crystallographic data in CIF format for compounds **1**, **4**, **5**, **7**, and **8** and Figures S1−S15. This material is available free of charge via the Internet at http://pubs.acs.org.

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