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The role of temperature in the synthesis of hybrid inorganic–organic materials: the example of cobalt succinates†

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Five different cobalt succinate materials synthesized from an identical starting mixture using temperature as the only independent variable show increasing condensation and density at higher synthesis temperatures.

The attraction of combining properties from both inorganic and organic components[1] has led to a surge of research directed at the synthesis of new hybrid materials with potential applications in catalysis,[2] gas storage,[3] and separations.[4] One major obstacle to the utilization of hybrid solids remains their poor thermal stability. We have previously shown that the thermal stability improves considerably for hybrid materials containing extended metal–oxygen–metal (M–O–M) arrays.[5] We call such materials hybrid metal oxides.[2] While it is well-known that hydrothermal synthesis conditions are more likely to result in extended M–O–M networks, there have been, surprisingly, no systematic studies on the role of synthesis temperature as an isolated reaction variable.

Cobalt succinates represent an unusually well characterized family of transition metal dicarboxylates, with four structures currently reported that incorporate only water and/or hydroxide as additional components. The simplest material, $Co(H_2O)_4(C_4H_4O_4)$,[6] may be prepared at room temperature by evaporation of a solution of cobalt chloride, succinic acid, and base. Its structure is very similar to that of cobalt acetate,[7] consisting of isolated cobalt atoms that are octahedrally coordinated to four water molecules and two succinate bridges, resulting in a 1D coordination polymer. Comparable reaction mixtures treated hydrothermally result in markedly different structures, MIL-9,[8] MIL-16,[9] and $Co_6(OH)_2(C_4H_4O_4)_5\cdot 0.5H_2O$.[10] In these structures, far fewer of the coordination sites on the cobalt atoms are occupied by aqua ligands, which leads to incorporation of μ_3 hydroxide, increased coordination of cobalt by carboxylate groups, and increased sharing of oxygen atoms. Each of these features favors infinite M–O–M networks. However, because different reactants, stoichiometries, and pH values were used to synthesize each of these materials in previous experiments, it is difficult to rationalize what reaction conditions lead to the formation of a specific phase. Here we examine the role of temperature in the synthesis of cobalt succinates by demonstrating that a single starting mixture may be used to synthesize all of these cobalt succinate structures, as well as a fifth, previously unreported material, by varying only synthesis temperature.

A stoichiometric reaction[11] using cobalt hydroxide, succinic acid, and water in approximately a 1:1:28 ratio, heated under reflux, led to the formation of a new phase which was characterized using single crystal XRD.[12] The structure consisted of one-dimensional chains, similar to the known cobalt succinate phase obtained by slow evaporation, where isolated Co(II) ions were replaced with edge-sharing trimers bound by two additional succinate ligands (Fig. 1). A more thorough structural description, additional figures, and crystallographic details are included as electronic supplementary materials.† Because this new phase appeared to represent an intermediate between the known solution and hydrothermally synthesized phases of cobalt succinate, we investigated which phases would result at lower and higher temperatures. To our surprise, we were able to prepare the four previously reported phases in addition to the new phase from this starting mixture, with different phases forming at 60 °C, 100 °C, 150 °C, 190 °C, and 250 °C. In all but one case (190 °C), the resulting materials were phase pure as verified by X-ray powder diffraction. For the 190 °C phase, impurities of the low temperature phase were present at 180 °C, and the higher temperature phase at 200 °C. Consequently, we are confident that its placement in this series is correct.

The resulting series shows several very clear trends (Table 1 and Fig. 2). At the lowest temperature used (60 °C), the tetra-aquo phase favored by room-temperature solution chemistry forms. Increasing temperatures in this series lead to fewer coordinated water molecules per cobalt atom, increased edge-sharing connectivity, higher coordination numbers for carboxylate groups, and incorporation of hydroxide in phases formed above 100 °C. The amount of hydroxide incorporated into the structure does not appear to follow a clear progression, suggesting that structural considerations are more significant than temperature in determining the

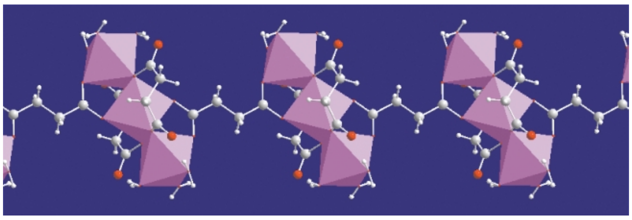

Fig. 1 The chain structure of $Co(H_2O)_2(C_4H_4O_4)$, with purple octahedra surrounding CoO_6 centers.

Table 1 Data for the five cobalt succinates synthesized in this series

Synthesis Temp.	Phase	H_2O/Co^{2+a}	Density g/cm^3	Co^{2+}/COO^-	$Co^{2+}/10^3$ Å^3	Dimensionality[b]
60 °C	$Co(H_2O)_4(C_4H_4O_4)_2$	4(4)	1.945	1	4.74	1(0)
100 °C	$Co(H_2O)_2(C_4H_4O_4)_2$	2(2)	1.926	2	5.50	1(0)
150 °C	$Co_4(H_2O)_2(OH)_2(C_4H_4O_4)_3\cdot 2H_2O$	$1(\frac{1}{2})$	2.085	2.67	7.28	2(2)
190 °C	$Co_6(OH)_2(C_4H_4O_4)_5\cdot{}_2H_2O$	$\frac{1}{3}(0)$	2.197	2.8	8.05	3(2)
250 °C	$Co_5(OH)_2(C_4H_4O_4)_4$	0(0)	2.337	3	8.88	3(2)

[a] The first number in the *H_2O/Co^{2+}* column refers to total water content, the second in parenthesis refers to water molecules coordinated to cobalt centers.
[b] The first number in the *Dimensionality* column refers to the total dimensionality, the second to the M–O–M dimensionality.

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† Electronic supplementary information (ESI) available: Crystallographic description of $Co(H_2O)_2(C_4H_4O_4)$, additional figures, single crystal X-ray refinement experimental details and tables. See http://www.rsc.org/suppdata/cc/b3/b311156c/

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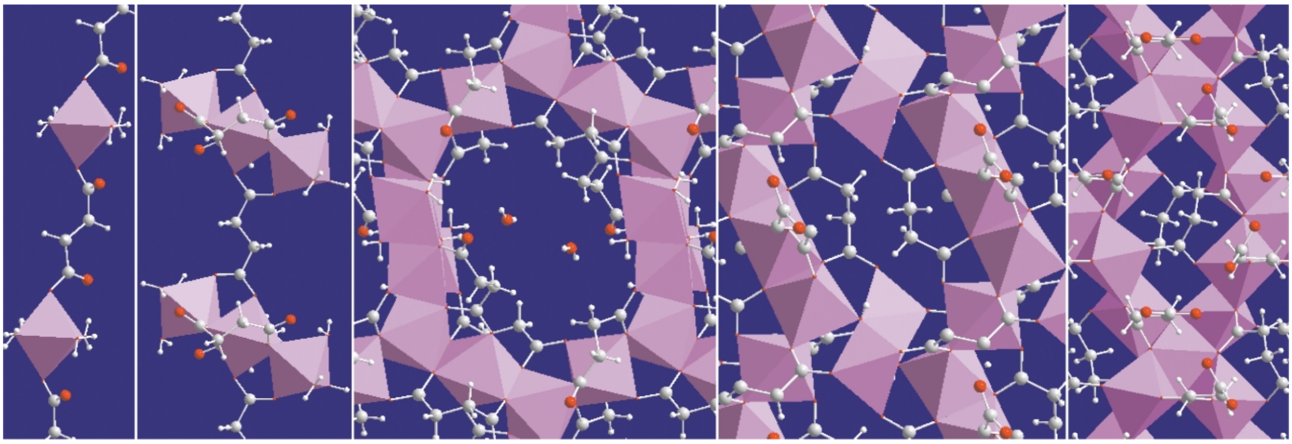

Fig. 2 Progression of the five phases of cobalt succinate, from low temperature (far left) to high temperature (far right).

overall stoichiometry. However, it is very clear that the amount of water in this series, whether total water or only water coordinating to cobalt atoms in the framework, decreases with increasing temperature. In both cases, the amount of water included in the final structure decreases for phases formed at progressively higher temperatures. Less water for phases formed at higher temperatures is likely driven by the increased entropic contribution associated with releasing H_2O from a confined state in these solids to a liquid state at higher temperatures. Because of the tendency for Co(II) to remain octahedral under synthesis conditions that are not strongly basic, the loss of coordinated water molecules must be compensated for by coordination of more cobalt atoms to each carboxylate group and increased sharing of coordinated oxygen atoms. These trends favor higher overall dimensionality as well as M–O–M dimensionality of the structures. In addition, the decreasing dielectric constant of water under hydrothermal conditions may also favor higher coordination numbers for carboxylate groups.[6]

These changes in the local coordination environment around cobalt have significant consequences in the overall structure. One trend that is qualitatively apparent in Fig. 2 is the increasing density of the metal–oxygen network. This correlation is apparent in the densities of the materials (Table 1), but is difficult to separate from the changing stoichiometries across this series. However, examination of the number of Co(II) atoms per 1000 Å^3 (Table 1) shows a remarkably clear increase that should be less sensitive to changes in composition. The cobalt density increases by roughly a factor of two over the temperature range studied, and continues to increase with rising temperature regardless of whether the hydroxide/cobalt ratio increases or decreases in the series. Qualitatively, this can be easily seen in the structures as presented in Fig. 2.

The overall dimensionality of the structures in this series also increases, with 1D chains up to 100 °C, 2D sheets at 150 °C, and 3D materials at 190 °C and above. The M–O–M dimensionality increases as well, beginning with isolated cobalt atoms or clusters through 100 °C, and continuing to 2D Co–O–Co sheets at 150 °C and above. However, it is likely that these changes are a consequence of the changing coordination around cobalt, as described above, and thus represent common trends, but with exceptions possible.

To our knowledge, this is the first study in which multiple metal–organic hybrid materials were synthesized by varying only temperature. While these observations are qualitatively apparent in many late transition metal hybrid systems, significant differences in synthesis conditions have heretofore made it impossible to clearly separate temperature from other factors. The existence of an unusual number of well-characterized cobalt succinate compounds enabled this study to reveal a clear relationship between synthesis temperature and structure. We are currently utilizing this system to explore other parameters, including reaction time, with a view of establishing whether the reaction proceeds under thermodymanic or kinetic control.

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11 $Co(H_2O)_2(C_4H_4O_4)$ was synthesized by combining $Co(OH)_2$ (1.55 g, Alfa Aesar) and succinic acid (1.97 g, Aldrich) in 33.3 mL deionized water (1 Co: 1 $C_4H_4O_4$: 28 H_2O). The pink mixture was stirred under reflux for 24 hours and the product was separated by filtration, rinsed with 2-propanol, and dried in air. Powder X-ray diffraction indicates that the product is a single phase matching the simulated powder diffraction pattern based on the single crystal structure. The same starting mixture, heated for 71.5 hours to 60 °C, resulted in the previously reported room temperature phase. Hydrothermal reactions were carried out by heating approximately 9 mL of a mixture with identical stoichiometry for 20 hours at 125 °C, 150 °C, 180 °C, 190 °C, 200 °C, and 250 °C in 23 mL Teflon-lined Parr autoclaves. The resulting products were filtered and identified by powder X-ray diffraction as described above.

12 Crystal data for **[1]**: Pbca, *a*, = 9.9608(18) Å, *b*, = 14.688(3) Å, *c*, = 14.925(3) Å, R1 = 0.0307 for 2628 reflections with $I > 2\sigma$, 175 refined parameters. CCDC 221317. See http://www.rsc.org/suppdata/cc/b3/b311156c/ for crystallographic data in .cif or other electronic format.