

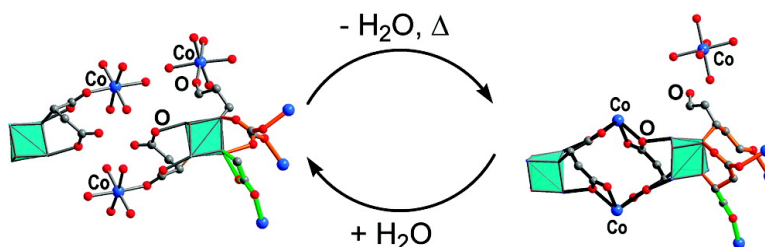
Communication

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## Reversible Single-Crystal-to-Single-Crystal Cross-Linking of a Ribbon of Cobalt Citrate Cubanes To Form a 2D Net

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We wish to report a heteromorphous, reversible single-crystal-to-single-crystal transformation involving cross-linking of a 1-D polymer of cobalt cubanes to form a 2-D net.

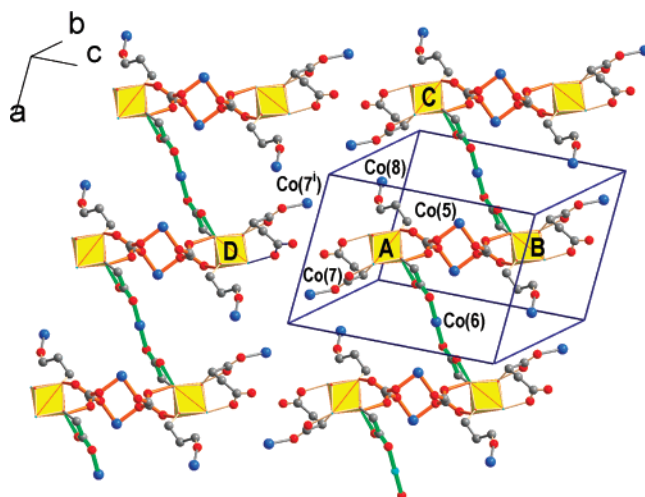
Thermally induced SC–SC transformations involving chemical reactions form an exiguous but promising body of research.<sup>1</sup> Particularly rare are reactions within the coordination spheres of transition metals. Such reactions are known in solids,<sup>2–4</sup> but they have often been accompanied by catastrophic failure of the crystal, thus preventing the identification of the products. The SC–SC coordination-sphere reactions that have been reported to date involve concerted molecular displacements,<sup>2</sup> or special movements such as Zn hopping inside channels,<sup>3</sup> or reversible bipy/MeOH substitution in the lattice of a Co(II) complex.<sup>4</sup>

Although photoinduced cross-linking reactions of organic and coordination polymers in solids are known,<sup>5</sup> to our knowledge there has been just one report of a *thermally* induced SC–SC transition with cross-linking of a transition metal-organic polymer to produce a 2-D net, and one 2D-to-3D transition.<sup>6</sup>

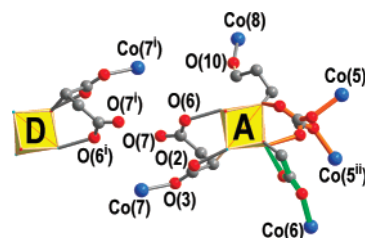
Molecular Co<sub>4</sub>O<sub>4</sub> cubanes are known<sup>7</sup> and some behave as single molecule magnets,<sup>8</sup> but only two polymers of discrete Co cubanes, both 3-D, have been observed.<sup>9</sup> (A 1-D chain of fused Co cubanes is also known.<sup>10</sup>) The majority of the known M<sub>4</sub>O<sub>4</sub> citrate cubanes have been characterized as their guanidinium salts.<sup>7</sup> We have developed a series of new products based on cobalt citrate cubane fragments, [Co<sub>4</sub>(citr)<sub>4</sub>]<sup>(8–)</sup> [citr = C<sub>6</sub>H<sub>4</sub>O<sub>7</sub><sup>(4–)</sup>], using wet chemistry techniques. Among them are several that appear to undergo thermally induced transformations in the solid state.

{Cs<sub>2</sub>[Co<sub>7</sub>(citr)<sub>4</sub>(H<sub>2</sub>O)<sub>13.5</sub>]}<sub>n</sub> **1** (Figure 1) is, to our knowledge, the first one-dimensional polymer of Co-cubanes and was prepared by the reaction of [Co(CO<sub>3</sub>)], H<sub>4</sub>citr, and CsOH. In the crystal, characterized by X-ray diffraction<sup>11</sup> at 278 K with the crystal in a stream of dry nitrogen, the polymer pitch corresponds to the crystallographic *a*-axis repeat. The basic unit of the polymer has two segments, with a doubly bridged pair of cubanes [A and B, Figure 1] forming one edge and with a single bridge (B···C) serving as the other. The ribbons thus formed lie side-by-side in the crystallographic (0, 1, –1) plane.

Co5, bound by two citrates, forms the double bridge with Co5<sup>ii</sup> (Figure 2). Co6, bridgehead of the single (B···C) link, lies on a crystallographic center of symmetry, thus with stoichiometry of 0.5 with respect to the cubane. The cubane (Co1–Co4), as well as Co5 and Co6, are not modified by the reaction (*vide infra*). Reaction occurs at Co7 and at Co8. Co7 is terminal, coordinated by oxygen atom O3 of citrate and by five water oxygen atoms. Co8 is also terminal, bound by one citrate oxygen, O10, and by five aqua ligands. Co8 lies on a general position, but has occupancy of 0.5, which was definitively established by the structure of **2** following the solid-state reaction. The aqua ligands at Co8 are also half occupied, with solvent water present the other half of the time.



**Figure 1.** Polymeric structure of **1**. Co blue, C gray, O red. Coordinated and uncoordinated water have been omitted.



**Figure 2.** Detail of the reactive zone of the structure of **1**. Symmetry codes: (i) 1–*x*, –*y*, –*z*; (ii) 1–*x*, 1–*y*, 1–*z*.

The stoichiometry of one repeat unit of polymeric **1** together with its associated interstitial water is C<sub>48</sub>H<sub>116</sub>Co<sub>14</sub>Cs<sub>4</sub>O<sub>98</sub> for {Cs<sub>2</sub>–[Co<sub>7</sub>(citr)<sub>4</sub>(H<sub>2</sub>O)<sub>13.5</sub>]}<sub>2</sub>·15H<sub>2</sub>O—two cubane units and 42 water molecules per unit cell.

Upon sitting for a day at 303 K in the dry nitrogen stream on the diffractometer, the crystal undergoes a nondestructive heteromorphous transformation involving a change of both the unit cell<sup>12</sup> and the chemical composition. The 1-D polymer of **1** is cross-linked to form the first 2-D polymeric net of Co cubanes, **2** (Figures 3 and 4). The *c*-axis of the unit cell changes significantly (Table 1). The planar polymer lies in the (0, 1, –1) plane of the new unit cell. If this plane were rigorously equivalent in the two structures, then the transition would be topotactic.

After the transformation at 303 K, one unit cell of **2** has a formula of C<sub>48</sub>H<sub>86</sub>Co<sub>14</sub>Cs<sub>4</sub>O<sub>83</sub> for [Co(H<sub>2</sub>O)<sub>6</sub>]{Cs<sub>2</sub>[Co<sub>6.5</sub>(citr)<sub>4</sub>(H<sub>2</sub>O)<sub>9</sub>]}<sub>2</sub>·3H<sub>2</sub>O. The Co7 congeners of two neighboring chains have each shed two Co7–OH<sub>2</sub> bonds and formed three new bonds to carboxylate oxygen from citrate—one such bond for each Co7 within its original chain and two to the neighboring chain—to form

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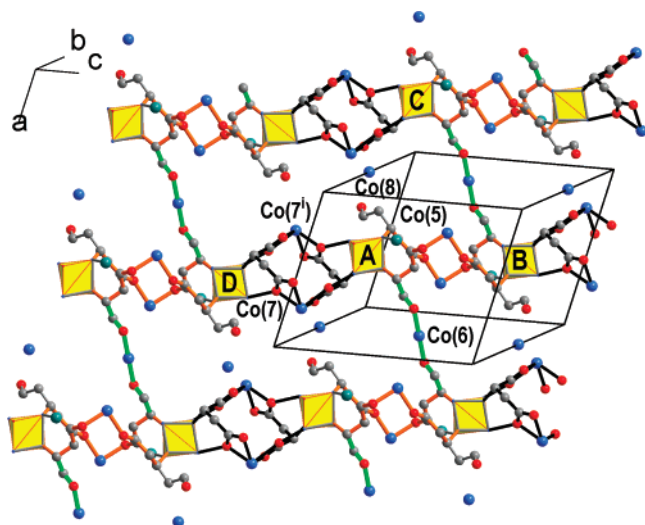


Figure 3. Polymeric structure of **2**, with atom colors as in Figure 1.

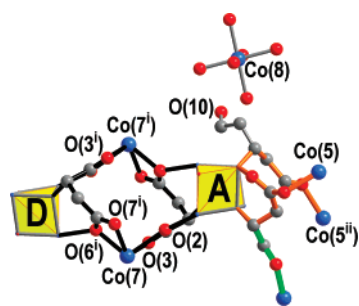


Figure 4. Detail of the crosslinked section of **2**.

Table 1. Evolution of Unit Cell Parameters with Temperature Cycling

	1	2	1'	2'
<i>T</i> , K	278(1)	303(1)	278(1)	303(1)
<i>a</i> , Å	11.5021(5)	11.4050(5)	11.4475(14)	11.3985(19)
<i>b</i> , Å	13.2108(9)	13.0515(9)	13.0936(15)	13.097(3)
<i>c</i> , Å	20.0315(13)	18.4855(9)	20.009(2)	18.451(3)
$\alpha$ , °	99.997(5)	101.734(5)	99.804(10)	101.805(16)
$\beta$ , °	91.157(4)	95.682(4)	91.258(10)	95.644(14)
$\gamma$ , °	114.800(5)	115.790(5)	114.939(12)	115.794(18)
<i>V</i> , Å <sup>3</sup>	2706.4(3)	2370.3(2)	2664.9(5)	2372.0(7)

a new double bridge cross-linking the originally independent polymers. Meanwhile, Co8 leaves the polymer, with the Co8–O10 bond breaking and one new Co–OH<sub>2</sub> bond formed. In **2**, Co8 lies on a crystallographic inversion center, perforce with stoichiometry of 0.5 relative to the cubane, thus confirming the stoichiometry determined for Co8 in **1**. The A...D distance of 11.6475(8) Å in **1** diminishes to 9.9565(6) Å in **2**.

Water egress in the transition amounts to 15 formulas per unit cell. Both structures possess a complex system of H-bonds, some strong, that must be implicated thermodynamically in the transformation.

After standing at ambient conditions for more than 2 months, the sample was re-examined and the unit cell (**1'** in Table 1) was found to have reverted to that of **1**.<sup>13</sup> The volume difference of some 40 Å<sup>3</sup> between **1** and **1'** suggests that water uptake in the reverse transition was not complete. As before, upon heating at *T* = 303 K in the nitrogen stream for a day, the crystal transformed to **2** as characterized by its unit cell (**2'**).<sup>14</sup>

In the one-dimensional polymer **1**, although the cubane core has S<sub>4</sub> symmetry, all four citrates are in fact chemically distinct at their

peripheries. One binds the bridgehead Co6. Two others are bound to the two congeners of Co5 that form the double bridge; and one of these also coordinates Co8. Another citrate binds Co7, in the reaction zone.

Half of the cubanes in **1** are bound to four peripheral Co atoms (Co5, Co5<sup>II</sup>, Co6, Co7) and half to five (the same four plus Co8). Citrate cubanes have previously been found with 2<sup>8b,15</sup> and 6<sup>9a</sup> peripheral metals, but not with four or five.

Co7 in **2** has an O<sub>7</sub> coordination sphere, with two four-atom chelates from two different citrates, plus three aqua ligands.

The most important feature of this transformation, however, is that it is a genuine *single sample* SC–SC transition.

These results demonstrate that thermally provoked SC–SC transformations can involve significant chemical rearrangement. We are presently examining further features of this process as well as other cubane-based systems that show signs of similar transitions. Such transformations in the crystalline state may occur more often than their frequency in the literature would suggest, because the potential for structural failure of the crystal can impede successful characterization of the products.

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**Supporting Information Available:** Preparation of **1**, CIF for the structures of **1** and **2**, details of the structure refinements. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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- (11) For **1**, *T* = 278(1) K, triclinic, *P*( $\bar{1}$ ), unit cell (Table 1) from 8228 data. Refinement: 12337 data, 808 parameters, *R*1 = 0.0584, *wR*2 = 0.1576, *g.o.f.* = 0.973. A refinement was attempted using space group *P*1, but this revealed the same disorder described in the reported group, *P*( $\bar{1}$ ). Details are given in the Supporting Information.
- (12) For **2**, *T* = 303(1) K, triclinic, *P*( $\bar{1}$ ), unit cell (Table 1) from 10838 data. Refinement: 10793 data, 688 parameters, *R*1 = 0.0860, *wR*2 = 0.2174, *g.o.f.* = 1.095.
- (13) For **1'**, unit cell (Table 1) from 4237 data. At this point, the crystal was cracked at one end. The second component, indexed with 3288 data, gave cell parameters *a* = 11.4649(16) Å, *b* = 13.131(2) Å, *c* = 19.973(3) Å,  $\alpha$  = 99.905(13)°,  $\beta$  = 91.200(11)°,  $\gamma$  = 114.622(15)°, *V* = 2678.3(7) Å<sup>3</sup>.
- (14) For **2'**, unit cell (Table 1) from 2383 data. The second twin component, indexed with 1860 data, gave *a* = 11.387(6) Å, *b* = 13.102(9) Å, *c* = 18.466(9) Å,  $\alpha$  = 101.91(5)°,  $\beta$  = 95.71(4)°,  $\gamma$  = 115.50(6)°, *V* = 2377-(2) Å<sup>3</sup>.
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