

GEOMETRY AND REACTIVITY IN CRYSTALLINE SOLIDS FORMED BY TRANSITION METAL CITRATE CUBANES

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ABSTRACT

Transition metals (M) and quadruply deprotonated citrate (citr^{4-}) form complexes with $[\text{M}_4(\text{citr})_4]^{(8-)}$ structural building blocks that have at their cores an M_4O_4 unit with cubane topology. At the periphery of the $[\text{M}_4(\text{citr})_4]^{(8-)}$ unit is an icosahedron formed by twelve oxygen atoms with partial negative charges, to which metal atoms can bind in a number of ways to give products with discrete molecular structures or with 1-, 2-, and 3-D polymers in the crystalline state. In addition to geometrically regular and irregular shapes, some of these products also display reactivity in the solid state, with reversible chemical processes having been observed to change the dimension of the polymer or to produce ion transfer with structural modulation. The geometries of the products reported to date are analyzed systematically in this presentation, and the geometrical relationships between reactants and products in a topotactic solid-state reaction are explored in detail. Unusual solvent uptake and loss in some of these solids is described, with reference to the structural features which enable this behavior.

INTRODUCTION

Some years ago we began exploring the chemistry of transition-metal complexes with citrate as a ligand, with some urging from our colleagues Fernando Palacio and Javier Campo of the Aragón Materials Science Institute, who thought that the prochiral character of citrate could be harnessed to give chiral paramagnets and other chiral systems with interesting magnetic properties. This aspect of the chemistry has not yet materialized, but the citrate cubanes that emerged from this work have turned out to possess unexpected solid-state reactivity as well as their own interesting magnetic properties. In this presentation we focus on the crystal structures and solid-state reactivity of these systems.

The magnetic properties of transition-metal cubanes, and of citrate cubanes in particular, have been studied by Murrie *et al.*, [1], Murray *et al.*, [2,3] and others. [4] Our own work has added some useful results to this body of knowledge, but the general scheme of the magnetism of these systems had already been established by others.

Crystals of the citrate cubanes were to reveal a wealth of other behavior, however. We have encountered a variety of dynamic effects involving reactivity – chemical bond making and breaking – in these molecular solids. It is on this aspect of the chemistry of these compounds that we shall focus here. The solid state reactivity, whose origins seem clear as will be described below, produces varied results. In one case, a one-dimensional polymer is cross-linked reversibly into a 2D net. [5] In another system a discrete molecule is easily converted by cobalt hopping

into an unsymmetrical molecule with concomitant transformation of the original ordered crystal into a modulated phase.

In this presentation we shall explore the geometry of the citrate cubanes – they are more than simple cubanes – with special emphasis on the structural and topological properties that make them reactive. These systems have within them a variety of geometrical forms, and these can be characterized using existing geometrical and, where appropriate, distortion parameters.

For single-crystal-to-single-crystal transitions of the sort that we observe for some of the citrate cubanes, we will describe a means of relating the initial and final relative dispositions of the molecular fragments that take part in the reaction. This is a subject that our laureate for this Transactions Symposium, Bruce Foxman, has been talking about for many years. Our treatment in this presentation, which we apply to the 1D-to-2D polymer transformation mentioned above [5], is based on the ideas that Professor Foxman has expounded.

THE RICH GEOMETRY OF THE CITRATE CUBANES

We use the term "cubane" for any compound whose core consists of eight atoms that form a figure possessing the basic components of a cube – three mutually perpendicular two-fold or four-fold symmetry axes and four three-fold symmetry directions inclined at somewhere in the vicinity of 54.7° to the two- or four-fold symmetry elements. These criteria are treated rather loosely, and in practice the "cube" of a cubane can consist of any eight atoms which, when one does not require them to be of the same element, form a closed figure that looks something like a cube.

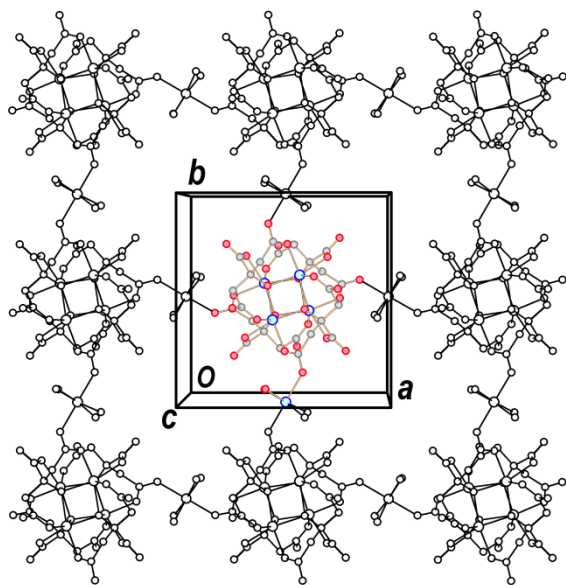


Figure 1.

cubane and surrounding ligands (in color) are linked to their neighbors in this case by bridging octahedrally coordinated Co(II) centers; one symmetry unique part of the bridge is also colored in the figure. This particular structure has bridges in two perpendicular directions, giving the square 2D polymer.

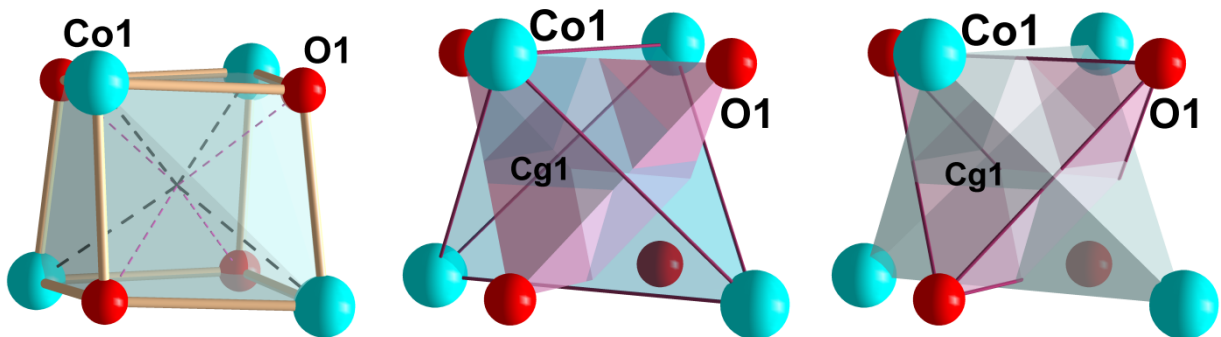


Figure 2.

At the heart of the structure is the cubane, of composition Co_4O_4 -- four Co(II) centers and four hydroxy oxygen atoms from as many quadruply deprotonated citrate ligands, which surround the cube as will be described presently. The cubane, shown in Fig. 2, consists of two interpenetrating tetrahedra. This unit can be connected so as to look like a distorted cube (Fig. 2, left), or it can be drawn as a "stella octangula," emphasizing the Co (center) or O (right) tetrahedra. The Co_4 tetrahedron is of notably larger dimension than is the O_4 figure.

The shapes of figures such as the tetrahedra of Fig. 2 can be characterized in terms of their distortions from ideal shapes, using their quadratic elongation parameter (Equation 1) and their tetrahedral angular variance (Equation 2). [7]

$$\langle \lambda_{tet} \rangle = \sum_{i=1}^4 (l_i / l_o)^2 / 4 \quad (1)$$

$$\sigma_{\theta}(tet)^2 = \sum_{i=1}^6 (\theta_i - 109.47^\circ)^2 / 5 \quad (2)$$

The tetrahedral quadratic elongation parameter, Eq. 1, uses the ratio of the distance of a vertex from the center of the tetrahedron, l_i , to l_o , which is the corresponding distance in a regular tetrahedron with the same volume as the figure being characterized. The variance of the tetrahedral angles, Eq. 2, tends to exaggerate larger deviations from a regular shape and thus makes it easy to distinguish between regular and distorted figures. For the quite regular Co_4 and O_4 tetrahedra of Fig. 2, $\langle \lambda_{tet} \rangle$ has values of 1.002 and 1.001, respectively, while the corresponding values of $\sigma_{\theta}(tet)^2$ are 2.481 and 5.766 $^\circ^2$. (The units of the tetrahedral angular variance are degrees squared.)

One of the principal agents in the interesting properties of the citrate cubanes is the citrate ligand itself. It provides a structural context for the cubane which augments the possibilities for

synthesizing systems with solid-state reactivity and with magnetically interesting properties. Fig. 3 shows the cubane with one of the four citrate ligands that surround it. The hydroxy oxygen is at one corner of the cube. The short carboxylate leg of the citrate forms a chelate through O2 to a neighboring Co atom, and both of the longer methylenecarboxylate legs do the same (O4, O6). So there are three chelates involving each citrate -- one five-membered ring and two with six atoms each. Each of the carboxylate groups has just one of its partially charged O atoms bound to cobalt. That leaves the other -- for example, O7 in Fig. 3 -- free to engage in bonding and/or non-covalent interactions at the periphery of the unit. In this structure, O7 binds a non-cubane Co atom, Co2, which bridges cubanes to extend the polymer (*vide infra*).

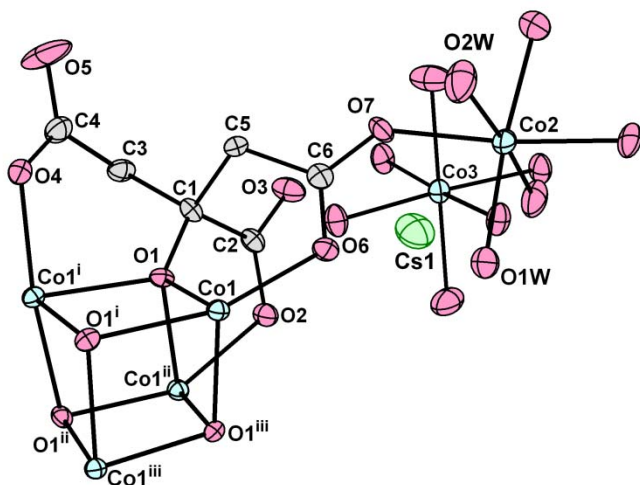


Figure 3.

date. Each citrate has a charge of (4-), and in this structure the cobalt centers are all Co(II); so the $\text{Co}_4(\text{citrate})_4$ fragment has a formal charge of (8-). Judicious choices of cations and crystallization conditions can be used to obtain structures with different overall shapes and dimensions, which in turn can give subtle differences in the magnetic properties of these systems, as reported recently. [8] This structure has the bridging $[\text{Co}(\text{H}_2\text{O})_4]^{(2+)}$ units, two per cubane, one independent $[\text{Co}(\text{H}_2\text{O})_6]^{(2+)}$ and two $\text{Cs}^{(+)}$ per cubane to balance the charge.

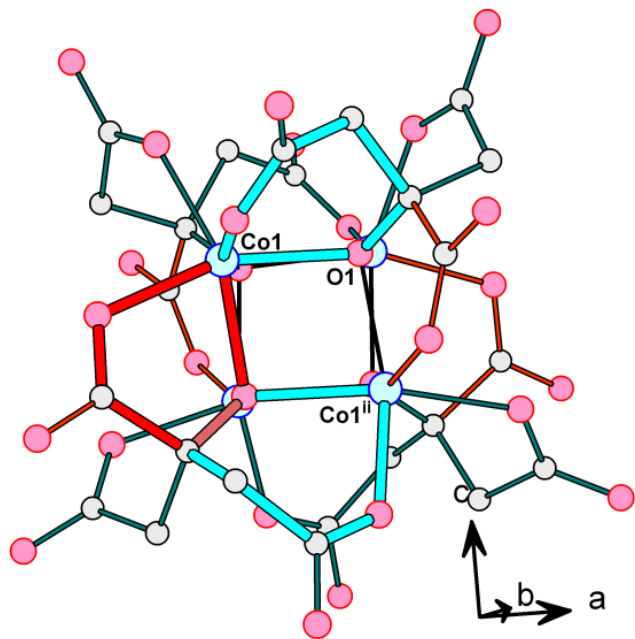


Figure 4.

Fig. 3 shows just one citrate. There are four around the cube, forming an arrangement with S_4 symmetry in all of the structures that we have observed to date. Each citrate has a charge of (4-), and in this structure the cobalt centers are all Co(II); so the $\text{Co}_4(\text{citrate})_4$ fragment has a formal charge of (8-). Judicious choices of cations and crystallization conditions can be used to obtain structures with different overall shapes and dimensions, which in turn can give subtle differences in the magnetic properties of these systems, as reported recently. [8] This structure has the bridging $[\text{Co}(\text{H}_2\text{O})_4]^{(2+)}$ units, two per cubane, one independent $[\text{Co}(\text{H}_2\text{O})_6]^{(2+)}$ and two $\text{Cs}^{(+)}$ per cubane to balance the charge.

While the four cobalt centers in the cube are responsible for a large part of the interesting magnetic properties that these systems possess, it turns out that from a structural and dynamic point of view, the interior of the cubane -- the part that looks like a cube -- is not its most interesting aspect. Fig. 4 shows the cubane with all four citrate ligands. The five-membered chelates gird the cube on its lateral edges, while the six-membered rings span the edges at the top and bottom in the figure. Each carboxylate, which has one of its oxygen atoms in the chelate ring with a Co(II) vertex of the cube, has its other oxygen atom, also partially negatively charged, pointing outward, where

it can bind further metal atoms or participate in hydrogen bonds, or both. These twelve peripheral oxygens confer upon this fragment the ability to enter into a remarkable diversity of structures and to participate in transformations in the solids thus formed.

These twelve oxygen atoms, taken on their own, form an icosahedron, which in this case is not the regular icosahedron that one can find in text books. This is a twelve-vertex figure with

twenty faces and 30 edges, an irregular icosahedron elongated along the four-fold axis of the crystal (the vertical direction in Fig. 4). Fig. 5 shows this three-dimensional figure, viewed along the tetragonal four-fold axis and emphasizing the oxygen atoms at the vertices. As drawn, the faces are all triangular, but there is no further similarity to a regular icosahedron. This figure has crystallographic S_4 symmetry, and the twelve oxygen vertices can be divided into three groups of four, each forming a tetrahedron with distinct geometry. There are four cobalt atoms attached to this polyhedron; these are the octahedrally coordinated cobalt atoms that bridge neighboring cubanes in the 2D net shown in Fig. 1.

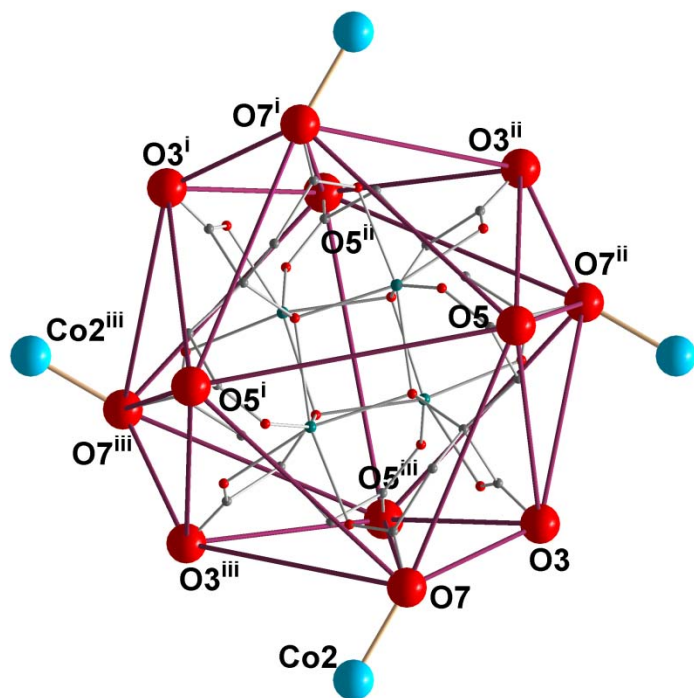


Figure 5.

It is instructive to examine the three concentric tetrahedra that can be extracted from this figure. Taking O5 and its three congeners, related by the crystallographic (-4) symmetry element, we can see that this tetrahedron is elongated along the crystallographic c -axis (Fig. 6a). The tetrahedron formed by O3 and its congeners is compressed along the same direction (Fig. 6b). However, the figure formed by O7 is quite regular (Fig. 6c), and it is here that the bridging Co(II) centers are attached. Co2 is attached laterally to O7, in such a way that the Co2 tetrahedron (Fig. 6d) is wider but not higher than the O7 figure. The geometry of Co2 attachment to the icosahedron, which can be seen in Figures 5 and 6, is such that the two Co2...Co2' edges that are perpendicular to the crystallographic c -axis, are perpendicular to each other. The propagation of the polymer thus follows two mutually perpendicular directions, which coincide with the a - and b -axes of the tetragonal cell (Fig. 1).

Table 1. Tetrahedral quadratic elongation and angular variance (deg^2) for peripheral O atoms in four Co citrate cubanes.

	$\langle \lambda_{tet} \rangle (O)$			$\sigma_{\theta}(\text{tet})^2 (O^2)$		
	O3	O5	O7	O3	O5	O7
this structure	1.3483	1.2247	1.0018	827.4987	882.0394	7.0677
Cs+	1.4100	0.9795	1.2523	918.9217	8.4082	979.3230
Rb+	1.3809	1.0023	1.2712	877.1153	8.8635	1044.7242
diamondoid	1.3367	1.0079	1.2301	808.8568	32.2729	901.2848

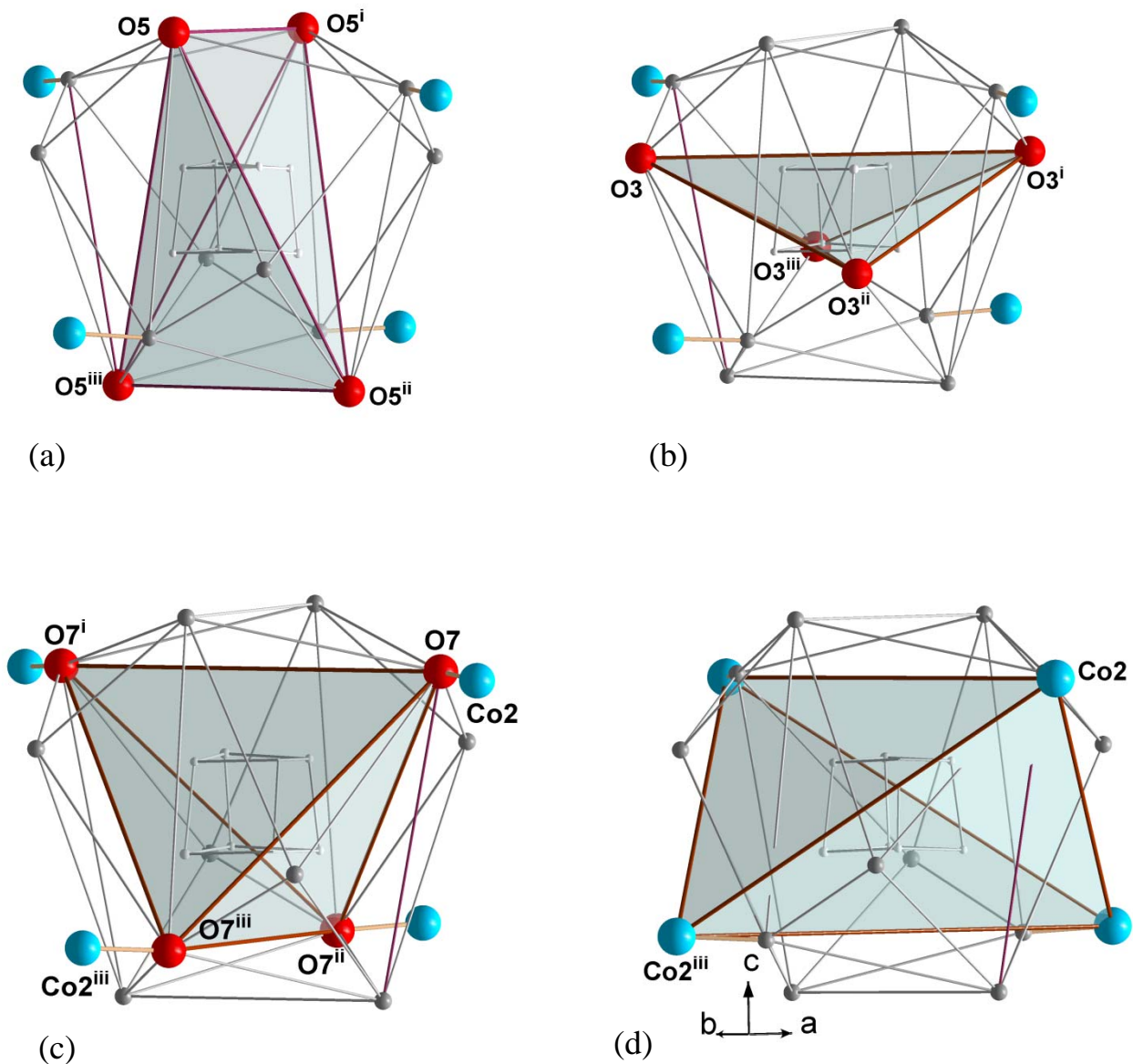


Figure 6.

Table 1 gives the distortion parameters for the tetrahedra formed by O3, O5 and O7, each with its symmetry relatives. The corresponding parameters are also given for the structures with the same anionic net but with $\text{Cs}^{(+)}$ or $\text{Rb}^{(+)}$ as cation. The row labeled "diamondoid" represents a structure with a 3-D polymeric net of Co citrate cubanes. (In these latter three structures, the names of O5 and O7 are reversed with respect to the structure described here. We have not changed the names in the table.)

This distorted icosahedron of electronegative oxygen atoms does not always attach metals in a symmetric fashion. In one compound that we have studied, [5] and which will be considered again below, successive cubanes were linked by a double bridge in one direction, by a single bridge in another, and each cubane also had two pendant $[\text{Co}(\text{H}_2\text{O})_5]^{(2+)}$ fragments attached to it, but not in any symmetrical fashion. Furthermore, not all of the cubanes that we have prepared form polymeric structures; we have observed discrete molecules and 1-, 2- and 3D polymers.

ORTHONORMAL REFERENCE FRAMES AND THE GEOMETRICAL RELATIONSHIP BETWEEN REACTANTS AND PRODUCTS IN SINGLE-CRYSTAL TRANSFORMATIONS

When single-crystal-to-single-crystal transformations occur, they are usually described in terms of the "before" and "after" conditions of the crystal. If the relative dispositions of the reactants are unchanged in the transformation, it is described as topotactic.

The reactions that we have encountered in transition-metal citrate cubanes may be called topotactic if one applies some lassitude to the definition of that term. In reality the relative dispositions of the reactants change in the single-crystal based reactions that we have observed. Among other things, the reactions are non-adiabatic and involve changes in the compositions of the crystals. Our reactions have invariably involved movement of, or some other change involving water molecules. In the 1D-to-2D polymer crosslinking that we observed some years ago [5], the reaction is provoked by dehydrating the crystal under mild conditions. The crosslinking occurs in the regions of the crystal abandoned by water, and it is accompanied by some collateral rearrangement of the structure – i.e., other than the crosslinking itself -- that also involves metal-ligand bond breaking and concomitant metal-aqua bond formation (a process called hydrolysis in other contexts).

We can provide a good description of the relationship between the "before" and "after" states in a single-crystal-to-single-crystal transformation, by using graphics derived from the individual phases. Alternatively, we can combine the atomic coordinates from the two phases and, choosing an appropriate common origin, we can analyze to some extent just how the atoms have moved with respect to each other. In this case we have to convert atomic coordinates from both the initial and final phases to an orthonormal reference system, because the unit cell will have changed in the case of a general transformation. It is this conversion to orthonormal coordinates that we shall consider next, because for a real, unmitigated single-crystal-to-single-crystal transformation – one whose initial and final phases are analyzed in the same crystalline sample – exact information on the relative dispositions of the two phases is available. With an appropriate choice of experimental conditions, namely using the same diffractometer and without removing the sample from its mount during the phase transition, the orthonormal reference frame of the diffractometer can be used as a common geometrical basis for the initial and final phases. As mentioned earlier, Bruce Foxman saw this possibility and has encouraged us to look into it.

Before describing how we have used this technique, for comparison we will first review the type of conversion to orthonormal coordinates that is usually used in crystal structure analyses. The most common need for orthonormal coordinates arises when one wants to draw pictures.

(Distance and angle calculations can be done using crystallographic coordinates in combination with the metric tensor.) For usual purposes, then, we are not comparing two phases, but rather simply converting our crystallographic coordinates to an orthonormal reference frame that can be understood by graphics plotters. This does not require that the original crystallographic reference frame be related to a laboratory reference system. A popular transformation is that which was described and derived in detail by Dunitz [9].

In relation to the crystallographic reference system \mathbf{a} , \mathbf{b} , \mathbf{c} , the orthonormal reference frame described by Dunitz, defined by vectors \mathbf{A} , \mathbf{B} , \mathbf{C} , has \mathbf{A} parallel to \mathbf{a} , \mathbf{B} in the \mathbf{ab} -plane and perpendicular to \mathbf{a} , and \mathbf{C} perpendicular to both \mathbf{A} and \mathbf{B} and disposed so as to form a right-handed system if \mathbf{a} , \mathbf{b} , \mathbf{c} are right-handed. The ORTEP manual [10] describes the same system succinctly as having its three axes parallel to \mathbf{a} , to $(\mathbf{a} \times \mathbf{b}) \times \mathbf{a}$, and to $(\mathbf{a} \times \mathbf{b}) = \mathbf{c}^*$. The transformation from fractional crystallographic coordinates (x,y,z) to Cartesian coordinates (X,Y,Z) is given by Equation 3, in which V is the unit-cell volume.

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} a & b \cos \gamma & c \cos \beta \\ 0 & b \sin \gamma & \frac{c(\cos \alpha - \cos \beta \cos \gamma)}{\sin \gamma} \\ 0 & 0 & \frac{V}{ab \sin \gamma} \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} \quad (3)$$

The inverse transformation from these orthogonal coordinates to fractional crystallographic coordinates is given by Equation 4.

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} \frac{1}{a} & \frac{-\cos \gamma}{a \sin \gamma} & \frac{bc(\cos \gamma \cos \alpha - \cos \beta)}{V \sin \gamma} \\ 0 & \frac{1}{b \sin \gamma} & \frac{ac(\cos \beta \cos \gamma - \cos \alpha)}{V \sin \gamma} \\ 0 & 0 & \frac{ab \sin \gamma}{V} \end{bmatrix} \begin{bmatrix} X \\ Y \\ Z \end{bmatrix} \quad (4)$$

For placing a crystal in a fixed, common reference frame that can be used for before-and-after structures, we can use a convenient transformation that is available in the context of any structure analysis with any modern single-crystal diffractometer. This begins with an instrument-fixed orthonormal reference frame, an example of which is shown in Fig. 7. The reference frame has its origin at the intersection of the rotation axes of the goniometer – that is, at the crystal. In the example shown in the figure, the x -axis of the orthonormal frame points to the x-ray source; the z -axis points up, and the y -axis completes the right-handed system. We should add here that we

For present purposes, we are more interested in the direct crystal lattice, whose analogous "real axis matrix" can easily be calculated beginning with the orientation matrix. In practice we begin with the orientation matrix, because that is readily available in diffractometer output. The columns of [UB] are Cartesian vectors and can be used directly in evaluating the kinds of expressions found in text books for direct and reciprocal cells (Equations 6,7).

$$\mathbf{V}^* = \mathbf{a}^* \cdot (\mathbf{b}^* \times \mathbf{c}^*) \quad (6)$$

$$\mathbf{a} = \frac{(\mathbf{b}^* \times \mathbf{c}^*)}{V^*} \quad (7)$$

The direct cell vectors and scalars are readily available through such expressions. Of particular interest is the real axis matrix, the analogue of [UB] in direct space, which relates coordinates in crystal space to the laboratory orthonormal reference frame, for the crystal orientation when all of the goniometer angles are set to zero (Equation 8). In the equation, lowercase (*xyz*) are fractional crystallographic coordinates, and uppercase (*XYZ*) are coordinates in the instrument-fixed orthonormal reference frame.

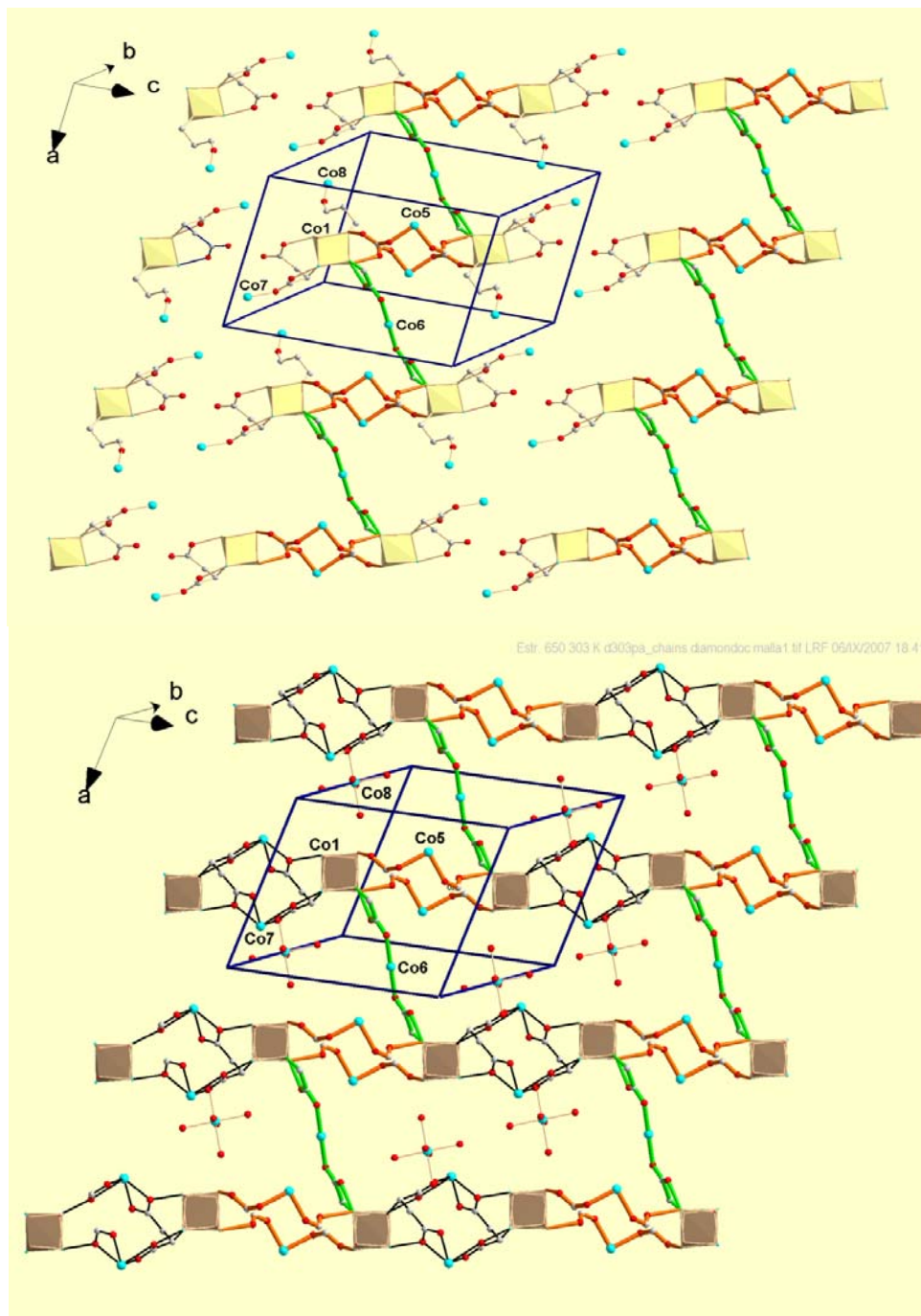
If a crystal has undergone a non-destructive transformation, so that [UB] can be determined before and after the change, and assuming that structural models can be extracted from diffraction data measured before and after as well, the atomic coordinates from both analyses can be transformed to the same orthonormal reference frame, that of the diffractometer, for comparison purposes.

$$\begin{bmatrix} X \\ Y \\ Z \end{bmatrix} = \begin{bmatrix} a_x & b_x & c_x \\ a_y & b_y & c_y \\ a_z & b_z & c_z \end{bmatrix} \begin{bmatrix} x \\ y \\ z \end{bmatrix} \quad (8)$$

COMPARISON OF CRYSTAL STRUCTURES BEFORE AND AFTER A SINGLE-CRYSTAL-TO-SINGLE-CRYSTAL TRANSFORMATION

We shall use an older example to illustrate the use of orthogonal coordinates derived from the real axis matrix in the comparison of the "before" and "after" structures of a crystal that undergoes a solid-state chemical reaction accompanied by a change of unit cell. In [5] we reported on the single-crystal to single-crystal transformation of a one-dimensional polymer of cobalt citrate cubanes, which can be provoked to undergo a cross-linking reaction in the solid to

produce a two-dimensional polymer whose single crystal structure can be analyzed by diffraction. Figure 8 shows the structures of $\{\text{Cs}_2[\text{Co}_7(\text{citr})_4(\text{H}_2\text{O})_{13.5}] \cdot 7.5\text{H}_2\text{O}\}_n$ **1**, $(\text{C}_{24}\text{H}_{58}\text{Co}_7\text{Cs}_2\text{O}_{49})_n$ and $\{[\text{Co}(\text{H}_2\text{O})_6]\{\text{Cs}_2[\text{Co}_{6.5}(\text{citr})_4(\text{H}_2\text{O})_9]\}_2 \cdot 3\text{H}_2\text{O}\}_n$ **2**, $(\text{C}_{48}\text{H}_{86}\text{Co}_{14}\text{Cs}_4\text{O}_{83})_n$. Compound **1** has a zig-zag chain of cobalt citrate cubanes, doubly bridged in one direction and singly bridged in another to form a serrate structure. The gaps between adjacent chains in Figure 8 (top) are occupied by unligated water molecules. With mild heating in a stream of dry nitrogen, a single crystal of **1** becomes a single crystal of **2**. In this process, pendant Co(II) centers of **1**



(Co7 and congeners) are ligated by citrate carboxylate oxygen atoms of the neighboring chain to give the 2-D polymer **2**. Another of the pendant Co centers of **1**, Co8, comes loose from its citrate ligand and takes on one more aqua ligand to become a $[\text{Co}(\text{H}_2\text{O})_6]^{2+}$ cationic complex. This transformation can in principle be made to take place in one crystal, without removing the crystal from the diffractometer. The 2-D polymer shown in Figure 8 (bottom) has two double-bridge systems in one direction and the original single bridge in the second dimension.

While the same crystalline sample was used for both of these structures, and the transformation was conducted on the diffractometer, in the actual event the crystal had been removed from the

Figure 8.

diffractometer (but kept on its pin) between the time of data collection for the first structure and the phase transition and second structure. If we use the orientation matrices [UB] for **1** and **2**, as determined by the diffractometer, to prepare orthogonal coordinates for use in a drawing with the two structures superposed in their orientations on the instrument, the result reflects the fact that the orientation of the crystal has changed (Figure 9, where gray represents the 1-D mother phase and red the 2-D, crosslinked daughter phase).

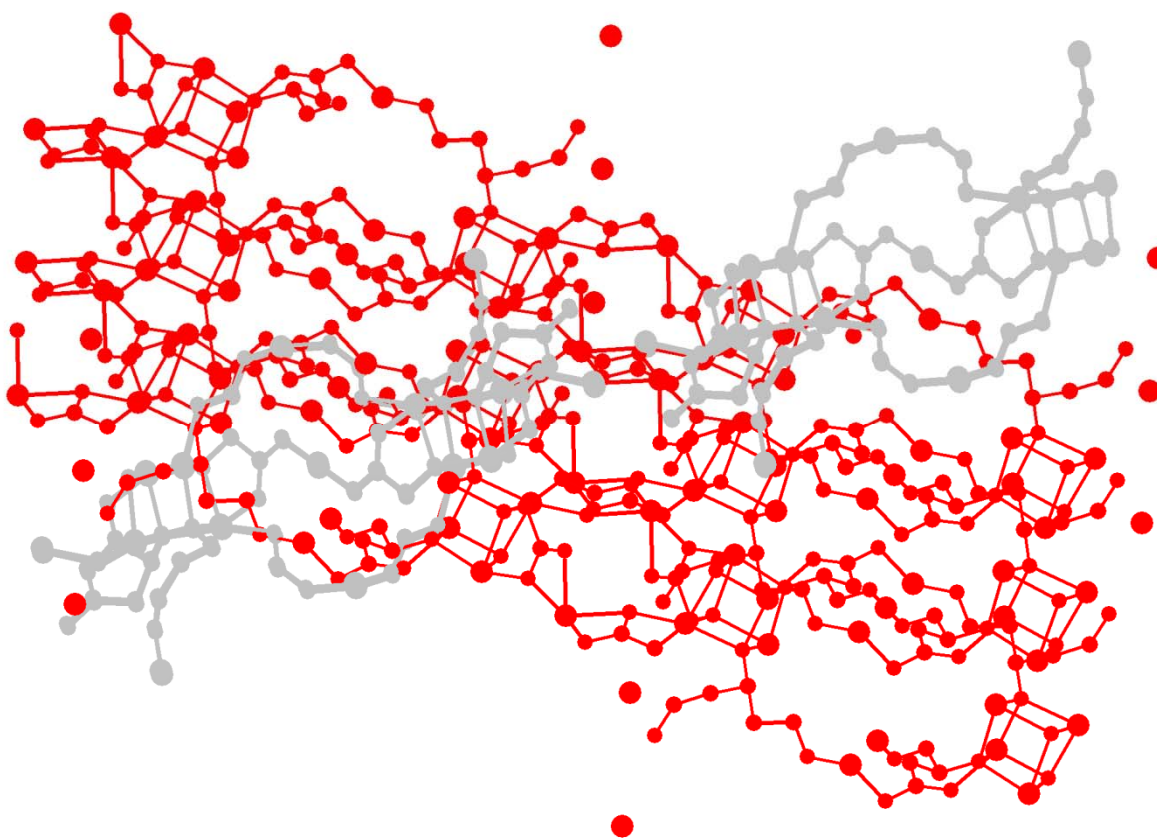


Figure 9.

With a simple assumption, the [UB] matrices can also be used to obtain a reasonable estimate of the relationship between the orientations of the sample before and after it was removed from the diffractometer. Since the crystal remained on its pin during the brief time that it was taken off the instrument, we can assume that the change of orientation when it was returned to the diffractometer consisted entirely of rotation about the laboratory z -axis. It is then easy to use the two orientation matrices to estimate the rotation angle. In this case, although there is a change in the crystal c -axis upon transformation, we were able to estimate with confidence, using a local computer program, that the change in orientation consisted of a 39.6° counterclockwise rotation of the pin on the goniometer head. On the basis of this estimation, a superposition of drawings of the two structures, Figure 10, is much closer to the picture expected for a topotactic reaction. In Figure 10 gray represents the original phase, the 1-D polymer; and red is the structure after the

crosslinking reaction. The contraction of the distance between the original chains is clear in both in-plane and longitudinal views.

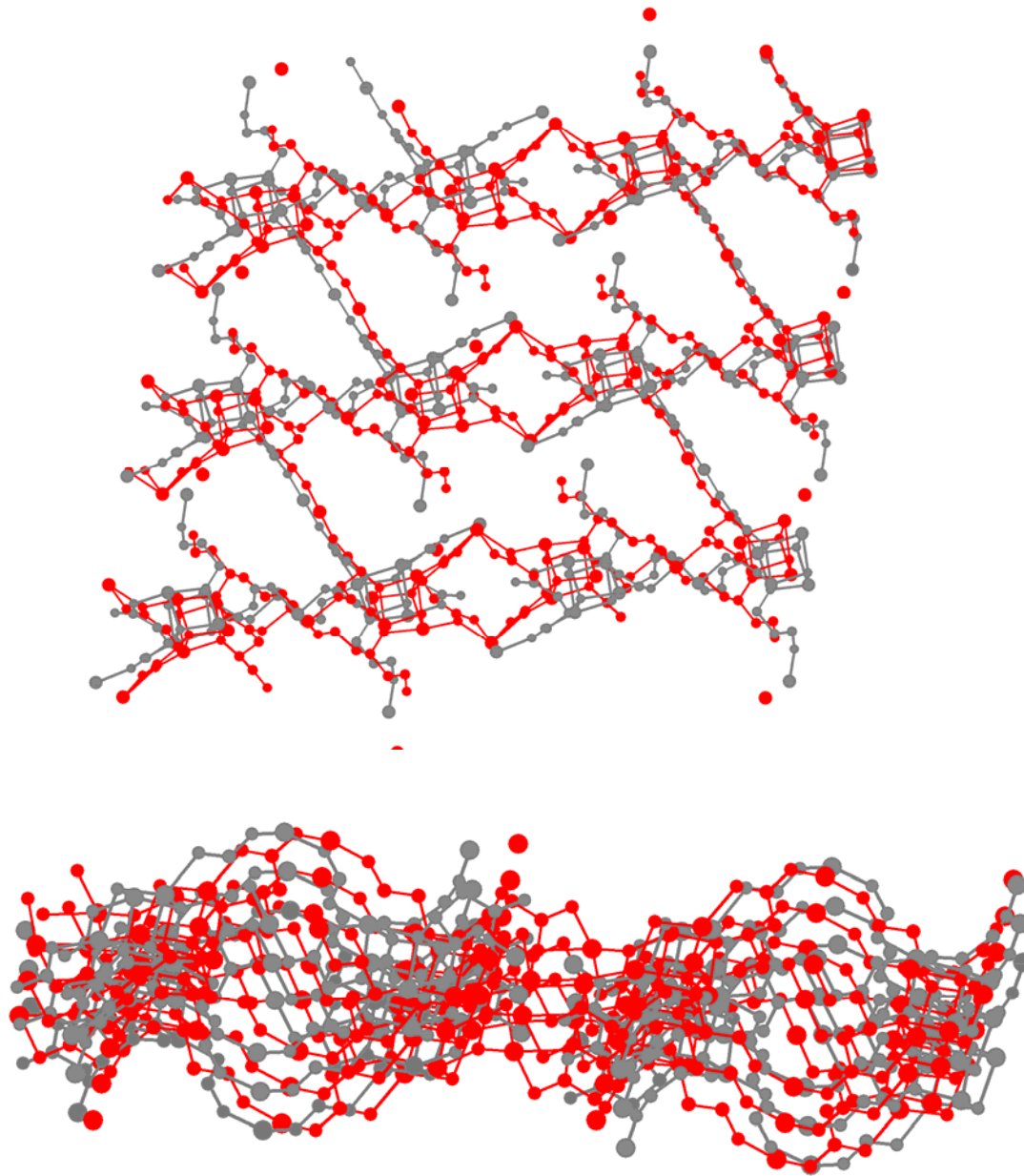


Figure 10. The mother (gray) and daughter (red) phases in the transformation of the 1-D polymer of Co citrate cubanes, $\text{Cs}_2[\text{Co}_7(\text{citr})_4(\text{H}_2\text{O})_{13.5}] \cdot 7.5\text{H}_2\text{O}$ **1**, to a 2-D crosslinked derivative, $\{[\text{Co}(\text{H}_2\text{O})_6]\{\text{Cs}_2[\text{Co}_{6.5}(\text{citr})_4(\text{H}_2\text{O})_9]\}_2 \cdot 3\text{H}_2\text{O}\}_n$ **2**. The orientations of the two compounds were derived exclusively on the basis of their orientation matrices on the diffractometer.

The important feature of the superposed pictures in Figure 10 is that the orientations of mother and daughter phases have been derived exclusively from their orientations on the diffractometer. No coordinate fitting has been done. This method of comparing the before- and after- pictures of a crystal that has undergone a single-crystal to single-crystal transformation, which was suggested by Bruce Foxman, gives a clean experimental view of the relationship between the two phases.

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