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Molecular composites based on first-sphere coordination of calcium ions by a cyclodextrin

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epoc ABSTRACT: Two organic-inorganic composites based on first-sphere coordination of calcium ions by α-cyclodextrin, highlight the possible creation of different architectures, even when involving identical molecular building blocks *and* inorganic clusters. In both forms, the mineral and organic matrices form separate motifs, with 40% of the crystal structure occupied by the mineral components. Copyright © 2000 John Wiley & Sons, Ltd.
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KEYWORDS: cyclodextrin; calcium coordination; molecular composites

Recently, solid-state complexes of cyclodextrins with salts have been considered as models for organic–mineral composites.[1,2] In such molecular composites, two types of organization may be observed; in the first the organic and mineral matrices form interlaced substructures, as is the case for the complex from β-cyclodextrin with hydrated magnesium chloride;[1] in the other, the two matrices occur as separate substructures, as described for the structure of the complex from α-cyclodextrin with potassium silicate.[2]

Structures of metal complexes have been reported previously for multideprotonated β- and γ-cyclodextrins[3,4] with Cu^{II} and Pb^{II} ions, respectively, and later for a series of α-cyclodextrinatocuprates.[5] The first structure in which undeprotonated cyclodextrin acts as a multidentate hydrogen-bond donor was described for the complex of β-cyclodextrin with calcium chloride.[6] In this complex, a distinct motif of mineral components was lacking. We report here on the first molecular composites based on first-sphere coordination of metal ions by an undeprotonated cyclodextrin.

The crystal structure of the α-cyclodextrin–$CaCl_2$ composite (**1**), of composition α-CD·3$CaCl_2$·19H_2O, monoclinic, space group $P2_1$, Z=2, a_1 = 13.293(5), b_1 = 15.947(2), c_1= 16.827(8) Å β_1 = 92.87(3)° 4536 unique reflections, 3280 observed with $I > 2\sigma(I)$, R_1 = 0.081, reveals two levels of organization. These are associations of molecularly hydrogen bonded α-cyclodextrin (α-CD) building blocks, leading to layers of 10 Å height (Fig. 1), and linkage of structural motifs of mineral components, which span the intermolecular gap to join the layers. This structural form contains water molecules of crystallization distributed over seven sites (only three of which have full occupancy). In addition, eight water molecules are coordinated to two cations (four for each), while the third cation is surrounded by water molecules positioned on 12 sites (only one having full occupancy). The molecular cavity contains only water molecules of crystallization on partially occupied sites.

The molecular building blocks are constructed from two α-CDs symmetry-related by the twofold screw axis. The α-CDs are strongly tethered by lateral hydrogen bonds (four per molecule) and covered on both hydrophilic sides by mineral components. This leads to a large sterically demanding local environment, which prevents strong molecular interactions between α-CDs from adjacent layers and generates intermolecular spaces large enough to accommodate well organized frameworks of mineral components.

All the ions are external to the cyclodextrin cavity but show direct interactions with the α-cyclodextrin matrix. One anion is positioned above the face of the primary hydroxyl groups and a second above the face of the secondary hydroxyl groups. The cations display two types of interactions. Two cations, Ca1A and Ca1B, are situated within the layers, in identical positions relative to two bidentate α-CD ligands. They adopt the same eightfold first-sphere coordination, Fig. 2(a), composed of four water molecules and four O atoms of two α-CDs (O-5/O-6 atoms and an O-2/O-3 pair of hydroxyls). These

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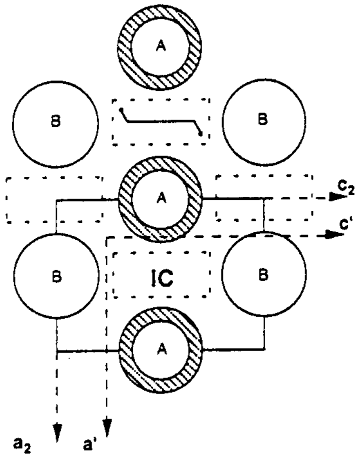

Figure 1. Schematic sketch of the molecular building block layer. The *a* and *c* in-plane dimensions of layers in **1**, appearing with an appropriate transformation of the unit cell, are: $a' = -b_1 = 15.943$, $b' = a_1$, $c' = a_1 + c_1 = 21.960$ Å, $\alpha' = 130°07'$. Each layer comprises two alternate symmetry-related rows of α-CDs, each being constructed from A or B molecules which have molecular sixfold axes perpendicular to the layers, with primary faces directed up (A) and down (B). The clusters are intercalated between four α-CDs. In **2**, the molecular layers are very similar with close *a* and *c* in-plane dimensions

cations are bridged, through their aqua ligands, by one anion and one water molecule of crystallization (WS), to form an inorganic cluster. The third cation is placed between the layers and presents a coordination environment predominantly composed of water molecules, the α-CD acting as an unidentate ligand, Fig. 2(b). For this cation (Ca2), two alternative, seven- or eightfold, first-sphere coordinations have been determined. They have in common two sites fully occupied by one secondary hydroxyl group and one water molecule, with either five (occupancy 0.6) or six (occupancy 0.4) water molecules on the remaining sites.

The stacking of the layers gives rise to oblique columns of 10 Å width, filled by mineral components (inorganic columns, **IC**); each **IC** being intercalated between four parallel columns containing α-CDs. The basic structural motif of **IC** is the inorganic cluster formed with Ca1A and Ca1B. Within an **IC**, clusters of adjacent layers, related by crystallographic translation, are linked through a second WS to give an infinite oblique chain which joins the Ca1A ions. The other two cations (Ca1B and Ca2) are anchored along this chain, through their aqua ligands (Plate 1). Several junction zones of mineral components, passing through aqua ligands of Ca2, interconnect **IC** columns.

Further information concerning the self-assembly of such organic/inorganic matrices was provided by the structure of a second 1:3 complex from α-CD with calcium chloride (**2**), with a nearby equivalent amount of water [$0.5(\alpha\text{-CD})\cdot 1.5CaCl_2\cdot 8.5(H_2O)$], orthorhombic, space group *I*222, $Z = 8$; $a_2 = 16.010(2)$, $b_2 = 20.380(2)$, $c_2 = 22.215(1)$ Å; 2960 unique reflections, 2604 observed with $I > 2\sigma(I)$, R_1=0.084; the parameters of three sites denoted Cl* have been refined as though a water molecule and a chloride anion shared the same site, with the same displacement parameters and occupancy factors

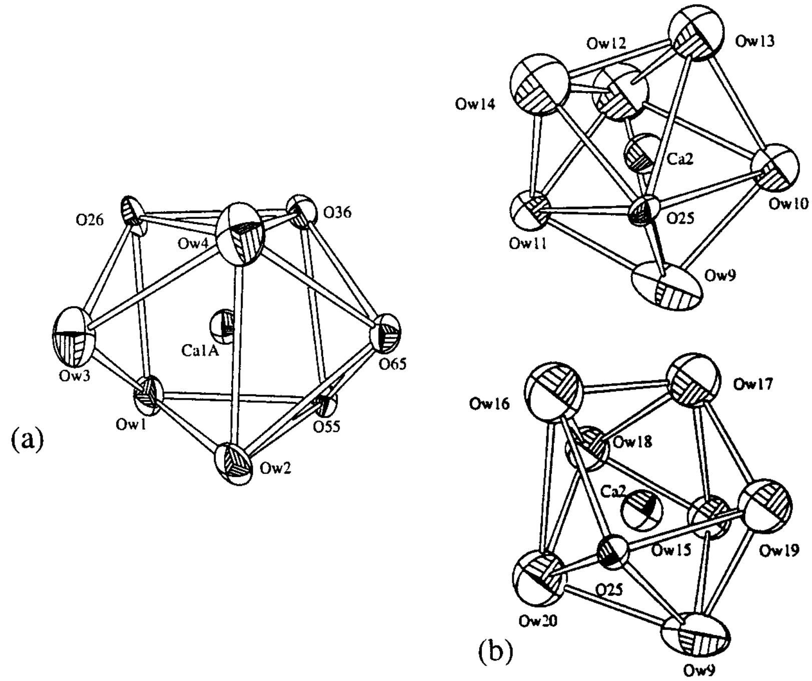

Figure 2. View of the coordination polyhedra of the calcium ions in **1**: (a) the environment of CalA; (b) the two alternative environments of Ca2

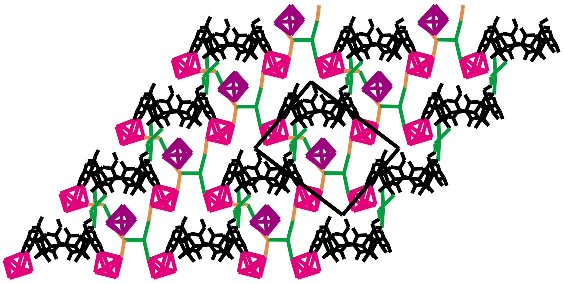

Plate 1. A section of the structure **1**, perpendicular to the layers (Calcium polyhedra, magenta (Ca1A and Ca1B) or violet (Ca2); chloride ions, green; water molecules of crystallisation, orange; cyclodextrin, black). Adjacent layers are transposed by about 7Å, forming oblique head-to-tail α-CD columns, with A (or B) molecules linked by two anions through primary and secondary hydroxyl groups. These columns are separated by the **IC**s columns. Parallel **IC**s are interconnected by junction zones that cross-link the chains of Ca1A by bridging clusters of adjacent layers through one anion, a WS, and aqua ligands of Ca2. As a result, each α-CD is surrounded by a chain-like loop of mineral components

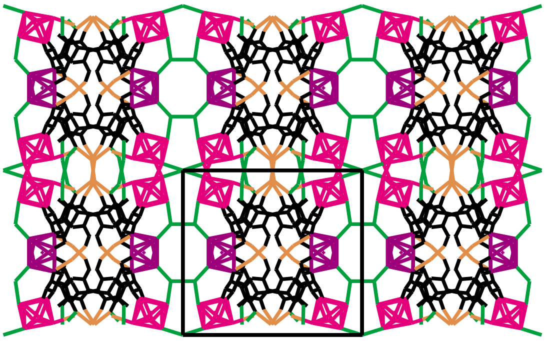

Plate 2. A section of the structure **2**, perpendicular to the layers (color scheme as in Plate 1). A and B α-CDs from adjacent layers, alternate in columns, with their secondary hydroxyl faces separated by a distance of about 7Å; they are connected by two doublets of symmetry-related WS molecules. The primary faces are held together through direct interactions with two Ca2 ions. In the **IC**s, two clusters related by symmetry are connected, at both sides, through Ca2; successive such double clusters, related by translation, are linked through aqua ligands of Ca1 and those of its symmetry counterpart. This gives rise to two interconnected infinite chains of calcium ions, perpendicular to the layers

of 0.5]. The molecular association in the layers is invariant (Fig. 1); the α-CDs and their environment display a real axial binary symmetry (the α-CDs are placed on twofold axes; the Cal ion adopts a similar first-sphere coordination to that observed in **1** for the CalA and CalB ions. Again, a cluster is formed: two symmetry-equivalent Cal are linked through a doublet of atoms on symmetry-quivalent Cl* sites. In contrast, the Ca2 ion and all the mineral components not involved in the clusters display different positions and interactions (the Ca2 ion is placed in a special position and presents an eightfold first-sphere coordination achieved with a pair of O-5/O-6 atoms, two atoms on Cl* sites and their symmetry counterparts). The resulting stacking mode gives rise to **IC**s perpendicular to layers. Here, the **IC**s contain the majority of ions and are not interconnected (Plate 2). They are intercalated between columns of head-to-head stacked α-CDs. Within the **IC**s, the mineral components present a highly symmetrical scheme in which symmetry-related clusters from adjacent layers are joined at both sides by interactions involving all calcium ions. This forms an extensive collaborative inorganic framework which gives rise to two infinite parallel chains of cations per **IC**.

These two types of self-assembling systems highlight the architectural modifications that arise simply from changes in the coordination environment and relative location of ions and water molecules external to the inorganic clusters. This is particularily the case for Ca2 which in **1** is located in the gaps between cyclodextrins, and in **2** is responsible for the organic column stacking and also is implicated in the **IC** structure.

When Ca2 is predominantly coordinated to water molecules, as for **1**, it just interacts through its aqua ligands, as parts of junction zones; it does not participate in the stability of the whole organization. The WS molecules, not hydrogen bonded to α-CDs, are essential in linking the clusters along and between the **IC**s; the anions are dispersed and are involved in the stability of α-CD columns and also the formation of junction zones. In this case, the α-CDs are partially encapsulated in an inorganic matrix (Plate 1). In complete contrast, when Ca2 is less hydrated, as for **2**, it simultaneously contributes to the cohesion of the α-CD columns, two α-CDs acting as bidentate ligands, and to the formation of the mineral substructure in **IC**s. The WS molecules are mostly excluded from **IC**s and trapped in α-CD columns, being fundamental to their stability, whilst the anions are now mainly confined in **IC**s. This results in an accumulation of ions which gives well structurally organized tubes of inorganic components exhibiting infinite chains of calcium ions, *not interlaced* with the organic columnar matrix (Plate 2).

In conclusion, we see that a relatively small degree of change in coordination about a single cation can transform the nanometer scale organization of mineral and organic components. Application of the solubility curves of cyclodextrin–salt systems[7] to systematic crystal growth experiments will allow a fuller determination of the structural motifs available from such molecular composites.

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