Zinc Saccharate: A Robust, 3D Coordination Network with Two Types of Isolated, Parallel Channels, One Hydrophilic and the Other Hydrophobic[**]

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Because of their availability and ease of functionalisation, sugar derivatives are attractive candidates as chiral building blocks for potentially useful polymers. Aldaric acids, which are polyhydroxydicarboxylic acids easily obtained from aldoses by terminal oxidation, could provide coordination polymers with interesting properties arising from the multiplicity of hydroxy groups and from the chirality. Considerable effort is now being made to lay the foundations for future "green" industrial production of chemicals and derived materials based on renewable starting materials and biodegradable products. Accordingly, the aldaric acid produced very simply from D-glucose, namely, D-saccharic acid (also known as D-glucaric acid) has been proposed as a potentially cheap and versatile commercial synthon, for example, in the manufacture of "hydroxylated nylons".[1] We are investigating the coordination polymers derived from aldaric acids with transition metals, lanthanides, and other metals; herein we report chiral zinc D-saccharate, which is exceptional in that its structure contains two types of parallel channels with very different characteristics, one type hydrophilic the other hydrophobic, which are isolated from each other by seemingly impenetrable walls. In 1998 it was shown that copper(II) saccharate has a linear polymeric chain structure,[2] and the structures of the potassium and calcium salts were described earlier.[3] The structures of a number of Group 1 and 2 metal derivatives of galactaric acid (also known as mucic acid) were reported (Na,[4] K,[4] Mg,[5] Ca[6] and Ba[6]). Galactaric acid is presently cheaper than saccharic acid, but is not chiral.

Crystals of hydrated zinc saccharate, $[Zn(C_6H_8O_8)]\cdot\approx 2H_2O$ (**1**), suitable for single crystal X-ray diffraction studies were obtained directly from an aqueous solution containing potassium hydrogen saccharate and zinc acetate.[7] All saccharate ligands are equivalent, their two carboxylate groups, although intrinsically different from each other, nonetheless play very similar structural roles. The zinc centers are chelated at both ends of the saccharate ligand by a carboxylate oxygen donor and an adjacent hydroxy group—O1a together with O2 at one end and O6a with O5 at the

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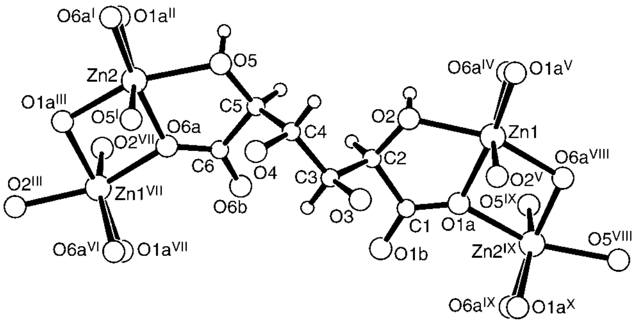

Figure 1. The attachment of the saccharate ligand to four zinc centers in **1** including the coordination environments of the zinc centers and the atom labelling. **I** *y*, *x*, 1−*z*; **II** 1.5−*y*, 0.5+*x*, −0.75+*z*; **III** 0.5+*x*, 1.5−*y*, 1.75−*z*; **IV** −0.5+*y*, 1.5−*x*, −0.25+*z*; **V** 1−*y*, 1−*x*, 1.5−*z*; **VI** *y*, *x*, 2−*z*; **VII** 1.5−*y*, 0.5+*x*, 0.25+*z*; **VIII** −0.5+*x*, 1.5−*y*, 1.75−*z*; **IX** −0.5+*y*, 1.5−*x*, 0.75+*z*; **X** 1−*y*, 1−*x*, 2.5−*z*.

other (Figure 1). The coordinated carboxylate-oxygen donors also bridge to another zinc center. Each ligand is therefore coordinated to four zinc centers, which are close to coplanar (Figure 1). There are two distinct types of zinc centers differing only slightly in their structural roles and chemical environments; both are attached to four ligands. The Zn1 atom is chelated by O1a and O2 from one ligand, and O1a^{V} and O2^{V} from another. The distorted octahedral coordination of Zn1 is completed by O6a^{IV} and O6^{VIII} from a further two ligands. Similarly, Zn2 is chelated by O6a and O5 from one ligand, and O6a^{I} and O5^{I} from another. The distorted octahedral coordination of Zn2 is completed by O1a^{II} and O1a^{III} from a further two ligands. A 3D four-connected net is thereby generated,[8] each Zn center being attached to four ligands and each ligand being attached to four zinc centers. A representation of the tetragonal extended network is shown in Figure 2. Two types of channels with very different characteristics, both of roughly square cross section, run parallel to the tetragonal axis producing, in projection, a pattern resembling a chessboard. All of the noncoordinated hydroxy groups project into one type of channel, a "hydrophilic channel". Each channel is defined and bounded by four roughly planar "walls", all of which are equivalent (Figure 3). All the noncoordinated hydroxy groups associated with a wall are found on one side. The walls are arranged so that the four surrounding a hydrophilic channel have all the noncoordinated hydroxy groups projecting into that channel. The four walls surrounding the other channels have the C–H bonds of C2 and C5 (see Figure 1 and Figure 2) of all the saccharate units projecting into the channel. As shown below, these nonhydroxylated channels, are able to accommodate nonpolar species, and are hence called "hydrophobic channels", despite the fact that they are able to accommodate water, albeit weakly. The hydrophobic channels can be regarded as infinite analogues of the hydrophobic cavities of the macrocyclic oligoglucose derivatives, the cyclodextrins, which have been intensively studied for decades on account of their ability to bind nonpolar species in the cavities. The chelate rings, which include the coordinated hydroxy groups, are roughly within the general plane of the wall. Zig-zag columns of alternating Zn1- and Zn2-type atoms running parallel to the tetragonal axis are found in the corners of the square channels where four walls conjoin. Every saccharate component of a wall is securely bonded to its two neighboring saccharate groups not only by the coordinate bonds but also by hydrogen bonds (open connections in Figure 3) between the noncoordinated carboxylate center of one and the coordinated hydroxy group of the neighboring saccharate group (O1b···O2, 2.60 Å and O6b···O5, 2.72 Å). These hydrogen bonds, which act as mortar between the saccharate bricks, no doubt contribute to the marked stability of the framework revealed in experiments described below.

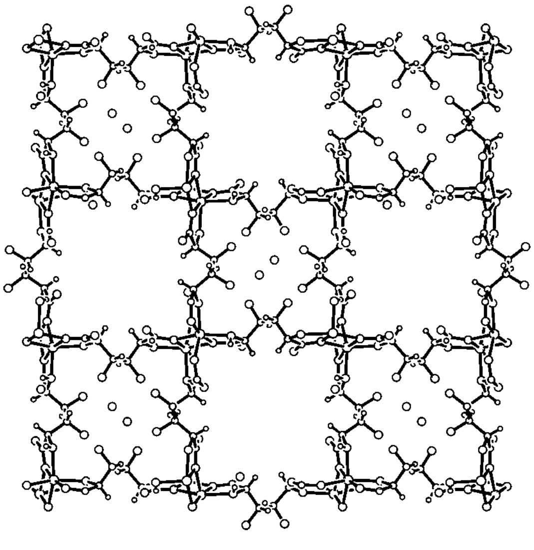

Figure 2. View down the tetragonal axis showing the two very different types of channels of roughly square cross-section in the structure of **1**. Well located water molecules in the hydrophilic channels are indicated.

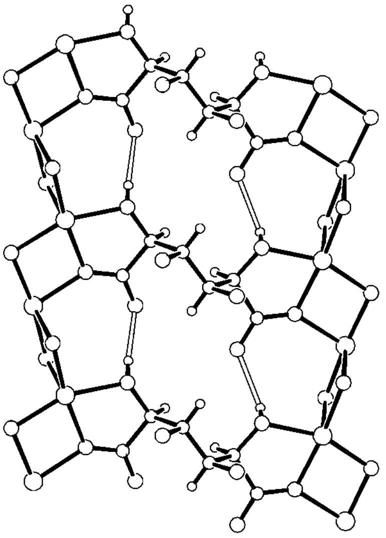

Figure 3. A wall as seen from inside a hydrophilic channel. The "open" connections represent hydrogen bonds cementing individual saccharate units into the wall.

The unit cell (Figure 2) contains two hydrophilic and two hydrophobic channels. All of the noncoordinated C=O groups associated with one hydrophobic channel in the cell point in one direction and all those in the other point in the other direction. The van der Waals free space for each of the two hydrophobic channels per unit cell (after the guest water molecules have been hypothetically removed) is approximately 200 Å^3 (averaged cross-sectional channel dimensions of approximately 5.8 × 5.8 Å).[9]

Elemental composition is consistent with about two water molecules per zinc atom or approximately 16 water molecules per unit cell (eight zinc atoms per cell). Water molecules, very well located in the structural analysis, are hydrogen bonded in the hydrophilic channels,[10] two for each channel in the unit cell (Figure 2). The remaining water molecules, approximately twelve, occupy the hydrophobic channels—approximately six for each of the two hydrophobic channels per cell. These water molecules are highly disordered and not well resolved in the structural analysis; however, the sum of their site occupancies is in good agreement with that indicated by the elemental analysis. As experiments described below indicate, this water in the hydrophobic channels is easily removed.

The thermogravimetric analysis of **1** shows three weight loss steps. Approximately 8 % weight is lost in the first step, which is already underway at room temperature and terminates abruptly at approximately 60 °C: we attribute this weight loss to the removal of water from the hydrophobic channels (calcd weight loss for the conversion of the dihydrate to the hemihydrate, i.e., the removal of water molecules from the hydrophobic channels with retention of water molecules in the hydrophilic channels, is 8.7 %). The amount of water in the hydrophobic channels is very temperature dependent at temperatures in the vicinity of room temperature, as indicated by the marked inclination of the mass versus temperature curve near room temperature (not shown). A second less abrupt decrease of approximately 3 %, attributed to loss of water from the hydrophilic channels, occurs in the ≈100–150 °C range (calcd weight loss for complete dehydration of the hemihydrate is 2.9 %). Major decomposition sets in above 270 °C.

A Lindeman glass tube containing a single crystal of **1** was put under vacuum, heated to 130 °C for 2 h, then cooled and sealed off. Single crystal diffraction character is retained after this treatment. The crystallographic structure analysis reveals the framework remains intact. The electron density in those regions of the hydrophilic channels where water molecules had been very clearly located prior to dehydration and also the electron density in the hydrophobic channels drops to very low levels. The ligand units, now liberated from the constraining influence of the hydrogen-bonded water molecules, show greater thermal motion and some degree of disorder. We consider it very significant that the crystal, after rehydration by exposure to the atmosphere, is returned to pristine condition, thus becoming indistinguishable in its diffraction behavior from the original hydrated crystal.

Crystals of **1** suspended in molten azobenzene at 96 °C for 4 h become uniformly yellow-orange. Azobenzene attached to the surface of the crystals was removed by thorough washing with toluene, then pentane. The IR spectrum shows azobenzene-derived bands at 776 and 689 cm^{-1}. Elemental analysis indicates the incorporation of approximately 0.8 molecules of azobenzene per unit cell, accompanied by the loss of water molecules from the hydrophobic channels. If the azobenzene molecules occupied the hydrophobic channels making end-to-end contact with each other, and if each were assigned an estimated van der Waals length of ≈14 Å, the unit cell, with a total length of hydrophobic channel available of 2 × 5.8 Å would be able to accommodate somewhat less than one molecule of azobenzene per cell (11.6/14 or ~0.8), which is in good agreement with the observation. The azobenzene-treated crystals retain good single crystal X-ray diffracting properties. The structural analysis reveals the zinc saccharate framework is essentially unchanged and hydrogen-bonded water molecules are well-defined in the hydrophilic channels, but the contents of the hydrophobic channels are highly disordered.

Upon exposure to I_2 vapor, crystals of **1** become deep red. The mass of a powdered sample of **1** exposed to I_2 vapor at 19 °C for five days increases by 16.6 % and thiosulphate determination of the I_2 content indicates the absorption of 0.30 molecules of I_2 per atom of zinc or 2.4 molecules of I_2 per unit cell. The observed mass increase is consistent with the displacement of all the water molecules from the hydrophobic channels (i.e. approximately 12 H_2O per unit cell) by the incoming I_2 molecules. A single crystal of **1**, after exposure to I_2 vapor retains its single crystal X-ray diffracting properties. The diffraction analysis reveals the zinc saccharate framework is essentially unchanged and the water molecules are still well defined in the hydrophilic channels. Large peaks of electron density within the hydrophobic channels are assigned to disordered iodine centers. The sum of the site occupancies indicates approximately 2.6 molecules of I_2 per unit cell, consistent with the gravimetric and chemical analyses.

Preliminary experiments indicate the incorporation of a range of other species into the hydrophobic channels, which include elemental sulphur, hydrocarbons, CCl_4 and CI_4. The existence of two types of channels with very different characteristics in the same network offers prospects of the simultaneous introduction of two different species into different channels, for example, ions of opposite charge, such as F^- into the hydrophilic channels and a range of cations into the hydrophobic channels. It is clear that zinc saccharate itself and metal derivatives of aldaric acids in general provide opportunities for novel chemistry, with realistic prospects of "green" applications.

Experimental Section

1: A solution of potassium hydrogen saccharate (0.164 g, 0.66 mmol) and zinc acetate tetrahydrate (0.148 g, 0.67 mmol) in water (3 mL) heated at 60 °C for 20 h deposited crystals of **1**, suitable for single crystal X-ray crystallography. Yield 0.143 g (70 %); elemental analysis (%) calcd for $C_6H_{12}O_{10}Zn$: C 23.3, H 3.9, Zn 21.1; found: C, 23.6; H, 3.2; Zn, 20.8.

Azobenzene inclusion: Crystals of **1** (102.0 mg, 0.330 mmol) were suspended in an excess of molten azobenzene and heated at 96 °C for 4 h. The resulting orange crystals were separated from the excess molten azobenzene and were thoroughly washed first with toluene, then pentane, and then dried in air. Mass of crystals retrieved 95.9 mg (97 %), elemental analysis (%) calcd for $C_{7.2}H_{10}N_{0.2}O_{8.5}Zn$ (i.e. $C_6H_8O_8 \cdot 0.5\,H_2O \cdot 0.1\,C_{12}H_{10}N_2$): C 28.7, H 3.3, N 0.93; found: C 28.3, H 3.1, N 0.91.

Iodine inclusion: Crystals of **1** (99.8 mg, 0.32 mmol) exposed to iodine vapor in a sealed jar containing excess iodine crystals for 140 h at 19 °C became dark red and the mass increased (to 116.4 mg). The iodine content was determined by adding an excess of sodium thiosulfate and back titrating with potassium iodate. Yield; elemental analysis (%) calcd for $[Zn(C_6H_8O_8)] \cdot 0.5\,H_2O \cdot 0.3\,I_2$: I, 21.2; found: I 21.2. The calculated mass increase for the conversion of $[Zn(C_6H_8O_8)] \cdot 2\,H_2O$ to $[Zn(C_6H_8O_8)] \cdot 0.5\,H_2O \cdot 0.3\,I_2 = 15.9\,\%$; observed mass increase = 16.6 %.

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[7] Crystals of $[Zn(C_6H_8O_8)] \cdot 2\,H_2O$, $[Zn(C_6H_8O_8)] \cdot 0.30\,(I_2) \cdot 0.5\,(H_2O)$, $[Zn(C_6H_8O_8)] \cdot 0.10\,(C_{12}H_{10}O_2) \cdot 0.5\,(H_2O)$ and $[Zn(C_6H_8O_8)]$ are all tetragonal, space group, $P4_12_12$. Crystal data for $[Zn(C_6H_8O_8)] \cdot 2\,H_2O$, **1,** $a = 19.0513(12)$, $c = 5.8265(8)$ Å, $V = 2114.7(3)$ Å^3, $T = 293$ K, $\rho_{calcd} = 1.944\,g\,cm^{-3}$, 2430 unique reflections out of 13262 relections measured, final *R* values, $R_1 = 0.0615$, $wR_2 = 0.1387$. Crystal data for $Zn(C_6H_8O_8) \cdot 0.30\,(I_2) \cdot 0.5\,(H_2O)$, $a = 18.9545(6)$, $c = 5.7911(3)$ Å, $V = 2080.6(1)$ Å^3, $T = 130$ K, $\rho_{calcd} = 2.290\,g\,cm^{-3}$, 2397 unique reflections out of 13297 reflections measured, final *R* values, $R_1 = 0.1030$, $wR_2 = 0.2488$. Crystal data for $Zn(C_6H_8O_8) \cdot 0.10\,(C_{12}H_{10}O_2) \cdot 0.5\,(H_2O)$, $a = 19.0427(6)$, $c = 5.8108(3)$ Å, $V = 2107.1(3)$ Å^3, $T = 293$ K, $\rho_{calcd} = 1.896\,g\,cm^{-3}$, 2429 unique reflections out of 13392 reflections measured, final *R* values, $R_1 = 0.1129$, $wR_2 = 0.2567$. Crystal data for $Zn(C_6H_8O_8)$, $a = 19.1245(8)$, $c = 5.7338(8)$ Å, $V = 2097.1(2)$ Å^3, $T = 293$ K, $\rho_{calcd} = 1.732\,g\,cm^{-3}$, 2410 unique reflections out of 13289 reflections measured, final *R* values, $R_1 = 0.1738$, $wR_2 = 0.3835$. All data were measured on a Siemens SMART/CCD diffractometer fitted with $Mo_{K\alpha}$ radiation. For all structures data were measured in the range $2° < \theta < 27.5°$. Empirical absorption corrections were applied using the SADABS program. Structures were solved using direct methods (SHELXTL V5.1[11]) and refined using a full-matrix least squares procedure based on F^2 (SHELX-97[12]). CCDC-197968–1949971 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

[8] The topology is related to but different from that underlying the PtS structure, which is also tetragonal and in which both the "square planar" and "tetrahedral" nodes have the Schlafli notation 4^28^4. In the net underlying the zinc saccharate structure there are three types of 4-connecting node, two having the point symbol 4^28^4 and one (the ligand) having the point symbol $4^28^310^1$.

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