

Hydrothermal syntheses and crystal structures of three zinc succinates: $\text{Zn}(\text{C}_4\text{H}_4\text{O}_4)\text{-}\alpha$, $\text{Zn}(\text{C}_4\text{H}_4\text{O}_4)\text{-}\beta$ and $\text{K}_2\text{Zn}(\text{C}_4\text{H}_4\text{O}_4)_2$

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Three zinc succinate coordination polymers have been synthesised hydrothermally. Two polymorphs of $\text{Zn}(\text{C}_4\text{H}_4\text{O}_4)$ adopt three-dimensional structures consisting of tetrahedral Zn atoms isolated from each other *via* bis-bidentate succinate moieties. The polymorphs differ in the conformation of the succinate group, the α form (**I**) having *syn*-periplanar geometry whereas the β form (**II**) has *anti*-periplanar geometry. $\text{K}_2\text{Zn}(\text{C}_4\text{H}_4\text{O}_4)_2$ (**III**) has a layered structure also composed of isolated tetrahedral Zn units. In this case the two crystallographically distinct succinate groups, one of each conformer, have bis-monodentate coordination, acting as both inter- and intra-layer bridges between neighbouring Zn-containing layers. The 'double' zinc succinate layers are separated along the *b*-axis by inter-layer potassium ions.

Introduction

Dicarboxylate ligands have recently been exploited to form a variety of metal-organic frameworks (MOFs), with the aim of producing some degree of 'zeolitic' host-guest behaviour. Yaghi and co-workers^{1,2} for example, have shown that it is possible to tailor the functionality and pore-size of these MOFs by systematic variation of the size and shape of the dicarboxylate group, R, around a central oxygen-centred tetrahedral Zn_4O group. Remarkable void volumes and methane adsorption capacities have been found in some of these materials. However, the exact nature of the host-guest behaviour in some zinc dicarboxylate polymers is complex, and still not fully understood. For example, within the zinc-1,4-benzenedicarboxylate system it has been shown that exchange of guest molecules such as water, DMF and methanol proceeds *via* framework collapse and subsequent recrystallisation rather than topotactic guest exchange.³ Yaghi's strategy for preparing the isoreticular zinc MOFs referred to above relies on pinpointing synthetic conditions which produce the stable Zn_4O core unit. Recently, a new strategy based on similar reasoning has been proposed by Zheng and co-workers.^{4,5} This substitutes the Zn_4O core by a larger, apparently more robust Zn_8SiO_4 core, wherein a tetrahedral silicate unit is encapsulated within a highly positively charged zinc 'shell'. This unit has been observed in both terephthalate and isophthalate polymers, both of which are thermally robust to an impressive 500 °C. We have attempted to follow similar reaction conditions in order to introduce this unit into further dicarboxylate complexes. Using succinate ($\text{C}_4\text{H}_4\text{O}_4^{2-}$) rather than the benzene dicarboxylates, produced the three title compounds; *i.e.* the Zn_8SiO_4 unit is not introduced into the products of the reactions under the conditions explored.

Experimental

All reactions were carried out under hydrothermal conditions at 180 °C, for 72 h in Teflon-lined stainless steel autoclaves. Six

reactions (summarised in Table 1) were carried out in total, using varying molar concentrations of sodium silicate solution (Aldrich, 27% w/w SiO_2), $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, succinic acid ($\text{C}_4\text{H}_6\text{O}_4$), KOH and H_2O . For the first three reactions no KOH was added, and the initial pH of the reaction mixture was about 3. For the latter three reactions, the pH was adjusted to 7 by addition of KOH.

Single-crystal X-ray diffraction studies were carried out on Bruker SMART or Rigaku Mercury CCD detectors with graphite monochromated Mo-K α radiation. Intensity data were collected using 0.3 or 0.5° steps to give at least a full hemisphere of coverage. All data sets were corrected for absorption *via* multiscan methods. Data analyses used the SHELXS and SHELXL packages. Details of the crystal structure determinations are given in Table 2. Powder X-ray diffraction data were collected on a Stoe STADI/P transmission diffractometer using Cu-K α_1 radiation.

CCDC reference numbers 197595–197597.

See <http://www.rsc.org/suppdata/dt/b2/b211181k/> for crystallographic data in CIF or other electronic format.

Results and discussion

From the six reactions carried out, three predominant crystalline phases were produced as shown in Table 1. These are designated $\text{Zn}(\text{C}_4\text{H}_4\text{O}_4)\text{-}\alpha$ (**I**), $\text{Zn}(\text{C}_4\text{H}_4\text{O}_4)\text{-}\beta$ (**II**) and $\text{K}_2\text{Zn}(\text{C}_4\text{H}_4\text{O}_4)_2$ (**III**). Selected geometrical features of each structure are presented in Table 3.

Phase (**I**) has been reported previously,⁶ and indexed correctly from powder diffraction data. However, no crystal structure has been reported. Our powder pattern of the bulk product matches that of PDF No. 51–2305, but contains some additional impurity phase, not yet identified. For (**II**) the phase purity of the product was confirmed by both elemental analysis (Found: C, 25.89; H, 2.08. Calc. for $\text{C}_4\text{H}_4\text{O}_4\text{Zn}$: C, 26.48; H, 2.22%) and by comparison of the experimental powder pattern

Table 1 Synthetic conditions (molar ratios) and products

Reaction	SiO_2^a	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	$\text{C}_4\text{H}_6\text{O}_4$	KOH ^b	H_2O	Product
1	1	10	10	N	1100	(II)
2	1	8	12	N	1100	(II)
3	1	12	8	N	1100	(II)
4	1	5	5	Y	1100	(I) + unknown
5	1	6.5	3.5	Y	1100	(I) + unknown
6	1	3.5	6.5	Y	1100	(III) + unknown

^a Relative molar ratio (added as sodium silicate solution). ^b Y = Added until pH = 7; N = not added.

Table 2 Crystallographic data for Zn(C₄H₄O₄)- α (I), Zn(C₄H₄O₄)- β (II) and K₂Zn(C₄H₄O₄)₂ (III)

	(I)	(II)	(III)
Formula	C ₄ H ₄ O ₄ Zn	C ₄ H ₄ O ₄ Zn	C ₈ H ₈ O ₈ K ₂ Zn
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	C2 (no. 5)	C2/c (no. 15)	I2/a (no. 15) ^a
<i>a</i> /Å	7.585(3)	6.922(4)	7.402(3)
<i>b</i> /Å	5.984(1)	6.787(4)	21.346(7)
<i>c</i> /Å	6.253(2)	11.267(6)	8.013(3)
β /°	108.51(3)	99.285(9)	106.26(3)
<i>V</i> /Å ³	269.1(2)	522.4(5)	1215.3(7)
<i>Z</i>	2	4	4
Crystal morphology	Plate	Block	Plate
Data collection temperature/K	293	125	293
Total/unique reflections	453/328	1211/380	2406/982
Ind. reflections (<i>I</i> > 2 σ (<i>I</i>))	326	376	655
Parameters	50	50	104
Final <i>R</i> 1, <i>wR</i> 2	0.023, 0.061	0.043, 0.121	0.041, 0.076
Flack parameter	0.20(4)		

^a The non-standard setting is chosen since the β angle is smaller.

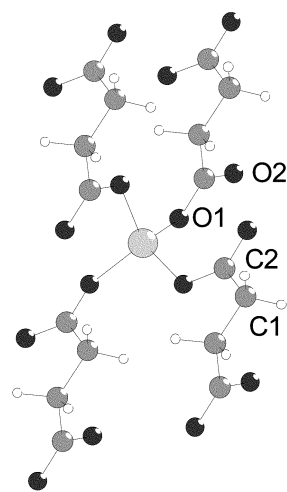
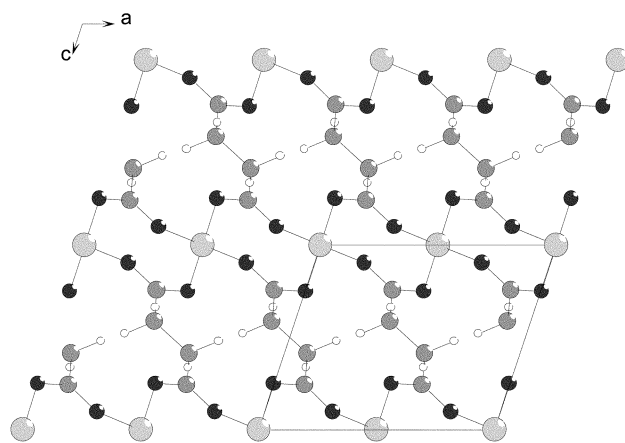
Table 3 Selected bond lengths (Å) and angles (°)

Zn(C ₄ H ₄ O ₄)- α (I)					
Zn1–O1	× 2	1.947(4)	O1–Zn1–O1	102.9(2)	
Zn1–O2	× 2	1.942(4)	O1–Zn1–O2	× 2	108.7(2)
C1–C1		1.523(9)	O1–Zn1–O2	× 2	114.9(2)
C1–C2		1.51(1)	O2–Zn1–O2		107.1(3)
C2–O1		1.259(7)			
C2–O2		1.263(7)			
Zn(C ₄ H ₄ O ₄)- β (II)					
Zn1–O1	× 2	1.958(3)	O1–Zn1–O1		105.0(2)
Zn1–O2	× 2	1.953(3)	O1–Zn1–O2	× 2	109.6(1)
C1–C1		1.53(1)	O1–Zn1–O2	× 2	117.4(1)
C1–C2		1.500(8)	O2–Zn1–O2		98.4(2)
C2–O1		1.266(6)			
C2–O2		1.269(6)			
K ₂ Zn(C ₄ H ₄ O ₄) ₂ (III)					
Zn1–O1	× 2	1.957(3)	O1–Zn1–O1		98.5(2)
Zn1–O3	× 2	1.968(3)	O1–Zn1–O3	× 2	107.2(2)
C1–C2		1.488(7)	O1–Zn1–O3	× 2	123.2(2)
C2–C2		1.51(1)	O3–Zn1–O3		99.5(2)
C3–C4		1.499(7)	K1–O2	× 2	2.663(4)
C4–C4		1.50(1)	K1–O4	× 2	2.713(4)
C1–O1		1.268(6)	K1–O4	× 2	2.724(2)
C1–O2		1.245(6)	K2–O2	× 2	2.743(4)
C3–O3		1.289(6)	K2–O3	× 2	2.841(4)
C3–O4		1.231(6)	K2–O3	× 2	3.081(4)
			K2–O4	× 2	3.109(4)

versus that calculated on the basis of the structure reported here. For (III), the powder pattern also showed a significant unidentifiable impurity phase.

The crystal structure of (I) consists of an infinitely connected three-dimensional framework constituted by tetrahedrally-coordinated Zn, with four different succinate ligands contributing one oxygen atom to four different Zn atoms, in bis-bidentate mode. The coordination geometry around the zinc centre is shown in Fig. 1. The succinate moieties lie on a two-fold axis and adopt the *syn*-periplanar conformation (*i.e. gauche* around the central C1–C1 bond, with a dihedral angle of $\sim 72.0^\circ$). The resultant network is shown in Fig. 2, along the *b*-axis. The space group necessitates a polar and chiral structure, with a continuous helical zinc succinate chain present along the *b*-axis (Fig. 3).

The crystal structure of (II) also consists of tetrahedrally-coordinated Zn, with four different succinate ligands contributing one oxygen atom to four different Zn atoms, in bis-bidentate mode (Fig. 4). However, in this case the succinate group lies on an inversion centre, and adopts the *anti*-periplanar conformation (*i.e. trans* around the central C1–C1

**Fig. 1** Zinc coordination environment in (I).**Fig. 2** Framework structure of (I) along [010].

bond, dihedral angle 180°). This results in a different three-dimensionally-connected framework, shown in Fig. 5. A feature of this centrosymmetric polymorph is a zinc succinate closed 'ring' rather than the 'chain' in phase (I). In the *b*-axis projection of (I) a similar 'ring' appears to exist, but this is, in fact, merely a projection of the helix in Fig. 3. These two projections are compared in Fig. 6.

If the overall network connectivities of (I) and (II) are compared, simplifying the succinate unit to a four-connected centre, it is possible to describe both as non-interpenetrating four-connected nets, with (I) representing a highly distorted

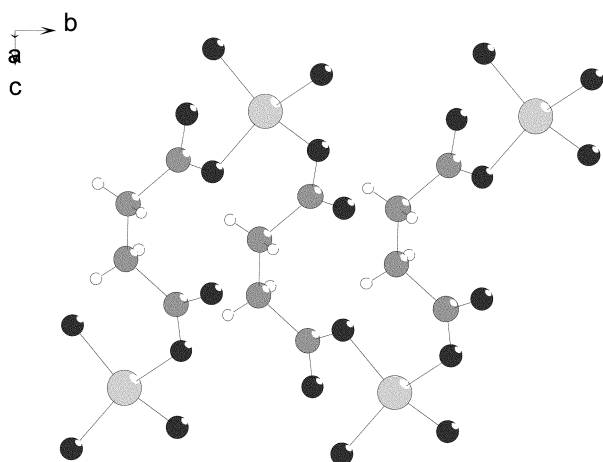


Fig. 3 Portion of the helical zinc succinate chain in (I).

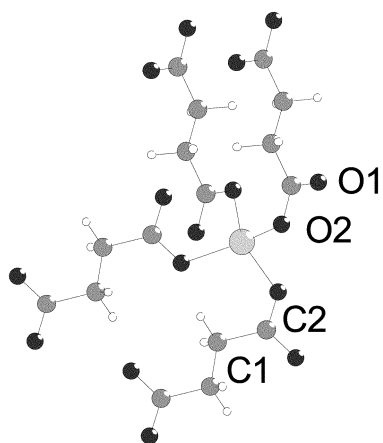


Fig. 4 Zinc coordination environment in (II).

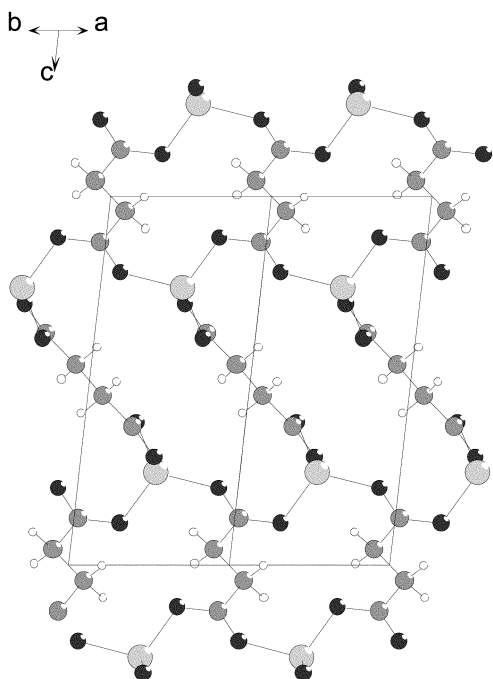


Fig. 5 Framework structure of (II) along [110].

diamondoid network and (II) adopting a PtS-type net, with the succinate moiety representing the square-planar centre.

Phase (III) is isostructural with the cobalt analogue $K_2Co(C_4H_4O_4)_2$ first reported by Livage *et al.*⁷ The structure consists again of tetrahedrally coordinated zinc centres, this time with

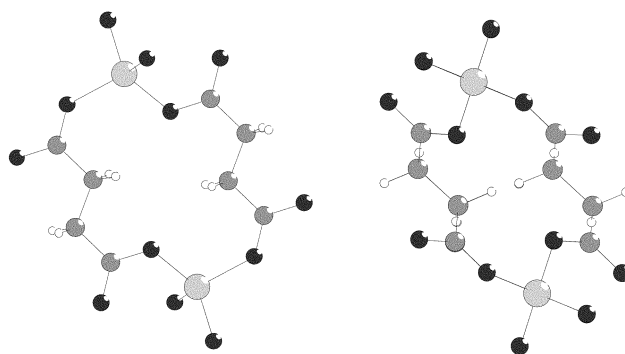


Fig. 6 Projections (along [010]) of the zinc succinate 'ring' in (II) (left) and the 'chain' in (I) (right).

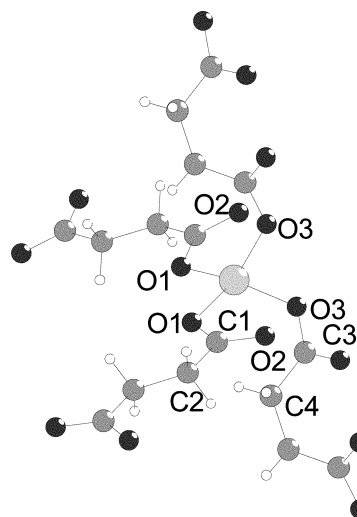


Fig. 7 Zinc coordination environment in (III). Note the two different succinate conformations, and the non-bonded Zn–O(2) interaction.

four different bis-monodentate succinate ligands (Fig. 7). There is an unusual structural feature, in that the next-nearest neighbour oxygen atom, O(2) is around 2.85 Å from Zn(1); whilst this certainly does not constitute a 'bond' in any real sense, it may suggest a very weak interaction, as shown by the slight lengthening of the four tetrahedral Zn–O bonds and the slightly more irregular tetrahedron, compared to phases (I) and (II), as evidenced in Table 3. Johnson and Harrison⁸ have recently reported unusual zinc coordination polyhedra in, for example, $SrZn(SeO_3)_2$, with abnormally long 'bonds' at 2.44 and 2.61 Å, in addition to the normal four short 'tetrahedral bonds'. The zinc succinate coordination network forms a two-dimensional sheet, which can be described as 'double layers' of zinc succinate, with the two crystallographically distinct succinate groups acting as both intra- and inter-layer linkages (Fig. 8). Interestingly, the two different succinate groups adopt contrasting *syn*- and *anti*-conformations, respectively (dihedral angles around C2–C2 = 180°, C4–C4 = 68.5°). The two crystallographically unique potassium ions separate the double-layers, to form an overall layered structure along the *b*-axis. The closest O–O separation between neighbouring double layers is ~4.3 Å.

In the above reactions we had attempted to incorporate the Zn_8SiO_4 core into an extended succinate network, utilising similar synthetic conditions to those of the benzenedicarboxylates recently reported. There is no direct evidence from the crystalline products we have obtained that this unit has been incorporated, although we cannot rule out trace impurity phases accommodating such a unit. Instead, two novel phases have been produced, along with a previously reported phase, which has now been structurally characterised. The synthetic conditions favouring either of the $Zn(C_4H_4O_4)$ polymorphs are presumably pH dependent (Table 1), though it is not clear why this

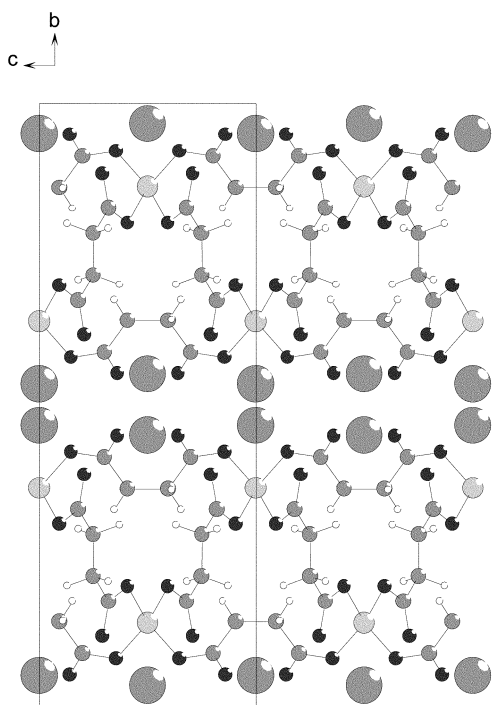


Fig. 8 Framework structure of (III) along [100].

should affect the preferred conformation of the succinate group. The formation of $\text{K}_2\text{Zn}(\text{C}_4\text{H}_4\text{O}_4)_2$ is favoured only in high concentration of both succinate and KOH.

Livage *et al.*⁷ prepared the Co^{2+} analogue, $\text{K}_2\text{Zn}(\text{C}_4\text{H}_4\text{O}_4)_2$, under non-hydrothermal conditions at room temperature. By a comparison of four known cobalt succinates they postulated several generalisations regarding the nature of the crystalline products formed under particular conditions. They suggest, in particular, that higher temperature (*i.e.* hydrothermal) conditions favour more condensation of the metal–oxygen lattice, and direct M–O–M linkages, rather than isolated metal sites

bridged by succinate, and also multidentate rather than monodentate coordination by the succinate ligand. Thus, edge-sharing MO_6 octahedra are seen in hydrothermally prepared $\text{Co}_5(\text{OH})_2(\text{C}_4\text{H}_4\text{O}_4)_4$,⁹ $\text{Co}_4(\text{OH})_2(\text{H}_2\text{O})_2(\text{C}_4\text{H}_4\text{O}_4)_3 \cdot 2\text{H}_2\text{O}$ ¹⁰ and also in $\text{Ni}_7(\text{C}_4\text{H}_4\text{O}_4)_6(\text{OH})_2(\text{H}_2\text{O})_2 \cdot 2\text{H}_2\text{O}$.¹¹ Very recently, Rao and co-workers¹² have used amine-templation to prepare several novel cadmium succinates, some of which also show some degree of Cd–O–Cd linkage. So far in the zinc succinate system we have no evidence for this type of metal–oxide condensation. Although guest molecules (*i.e.* H_2O) have not been incorporated into our materials, it seems likely, given the versatile guest-exchange behaviour of the benzenedicarboxylates already known, that use of other solvents within these systems will produce interesting behaviour, especially given our observation of different conformational polymorphs due to the increased flexibility of the succinate *versus* rigid dicarboxylates. Further synthetic work is planned in order to isolate such phases.

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