Preparation using metal oxide precursors and crystal structures of the copper and zinc vinylphosphonate materials $M(O_3PC_2H_3)\cdot H_2O$ (M = Cu, Zn)†

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Copper vinylphosphonate monohydrate, $Cu(O_3PC_2H_3)\cdot H_2O$, and zinc vinylphosphonate monohydrate, $Zn(O_3PC_2H_3)\cdot H_2O$, materials have been prepared using vinylphosphonic acid, and copper and zinc oxide, respectively, as precursors. Their crystal structures have been solved by single crystal X-ray diffraction and show that in copper vinylphosphonate, the Cu atoms are five-coordinate, whereas in zinc vinylphosphonate, the Zn atoms are in a distorted octahedral environment. In both structures, closest neighbour vinyl groups are separated by short contacts of *ca.* 4.15–4.3 Å. However, due to the different coordination environments of the metal centres, the orientation of the vinyl groups in these two structures is not the same, which is expected to lead to different solid state reactivity with respect to the possibility of dimerisation or polymerisation reactions.

Introduction

Different divalent metal phosphonates, $M^{II}(O_3PR)\cdot H_2O$, with M = Mg, Mn, Zn, Co, Ni, Cd, and R = alkyl or phenyl, have been reported[1–4] to be isostructural, crystallising in an orthorhombic unit cell, space group $Pmn2_1$, $a = 5.6–5.8$, $c = 4.7–4.9$ Å and with the b parameter varying according to the size of the organic group. Cunningham *et al.*[5] demonstrated the octahedral coordination of the metal from consideration of electronic spectra. Cao *et al.*[1] reported that, for all examples, the octahedral coordination sphere around each metal centre is built up as follows: four oxygen atoms are shared with other metal atoms (two of these oxygen atoms coming from the same phosphonate group and chelating the metal centre), a further unshared oxygen forms a direct link from the metal centre to the phosphorus only and the octahedral coordination is completed by the oxygen of the water molecule.

However, divalent copper phosphonates $Cu(O_3PR)\cdot H_2O$ differ from their analogues. Clearfield and Zhang (for R = CH_3, C_6H_5),[6] and Bujoli *et al.* (for R = C_2H_5)[7] described the layered structure of these compounds, formed by unusual 5-coordinate distorted square pyramidal copper atoms. Each copper atom is bonded to four coplanar oxygen atoms (3 oxygens from one phosphonate group and the other from the water molecule), while a fifth oxygen lies such that the Cu–O bond is nearly perpendicular to the plane and completes the pentacoordination.

We have been interested in the development of phosphonate materials containing vinyl functional groups, with a view to utilising the vinyl functionality for coordination of species, or for investigation of further organic reactions within the interlayer region. In this respect, the orientation/alignment of the vinyl groups within the structure may have an important effect on the reactivity. In a previous paper,[8] we presented the synthesis of a range of $Mg_{1-x}Zn_x(O_3PC_2H_3)\cdot H_2O$ compounds, synthesised *via* a melt method involving heating mixed metal hydroxides with the desired phosphonic acid above the melting point of the phosphonic acid.[3] During this study, we also found that it was possible to use metal oxides, *e.g.* ZnO, to obtain products with isomorphous structures. The microcrystalline/powdered nature of the products meant that although we were able to index the powder diffraction data (and identify that they fit in with expected trends), we were unable to carry out the full structural determination necessary to reveal the interaction between vinyl groups in the interlayer region.

Conventionally, most metal phosphonate materials are synthesised by crystallisation from an aqueous solution containing the phosphonic acid and a metal salt (usually the metal sulfate or metal nitrate), with addition of a source of base (hydroxide and/or urea) to control pH.[6,7] Here, we present the results of our studies, in which we show that it is possible to use metal oxides as precursors to the formation of phosphonate materials in aqueous syntheses as an alternative to the metal salts above. We have obtained copper and zinc vinylphosphonates by using copper and zinc oxide, respectively, as the metal sources. The structures of these materials have been successfully solved from single crystal X-ray diffraction data and demonstrate both the different coordination encountered for Cu and Zn within the structures, and the close approach of the vinyl groups, suggesting that it may be possible to carry out topochemical solid state reactions, such as dimerisation or polymerisation, within the interlayer region.

Experimental

Starting materials

Chemicals used were of reagent grade quality and were obtained from commercial sources. Zinc nitrate hexahydrate and copper nitrate hemipentahydrate were purchased from Avocado. Vinylphosphonic acid and urea (99%) from Aldrich were used without further purification.

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† Electronic supplementary information (ESI) available: rotatable 3-D crystal structure diagrams in CHIME format. See http://www.rsc.org/suppdata/nj/b2/b200438k/

Preparation of copper and zinc oxide precursors

Copper and zinc oxides were obtained using the following standard procedure: 100 ml of a solution containing copper(II) nitrate hemipentahydrate, $Cu(NO_3)_2 \cdot 2.5H_2O$, (9.30 g, 0.04 mol) or zinc nitrate hexahydrate, $Zn(NO_3)_2 \cdot 6H_2O$, (11.89 g, 0.04 mol) in distilled water were slowly dropped, with stirring, into 100 ml of 2 M sodium hydroxide solution.

Upon complete addition, the mixtures were refluxed for 6 h. The precipitates formed were then filtered off, washed thoroughly with distilled water until neutral and dried overnight in an oven at 60 °C.

Synthesis of $Cu(O_3PC_2H_3) \cdot H_2O$ (I)

Copper oxide (0.79 g, 10 mmol) with an excess of vinylphosphonic acid (1.40 g, 13 mmol) was dissolved in 20 ml of distilled water. Urea (3.12 g, 52 mmol, 4-fold excess over vinylphosphonic acid) was added and the brownish solution held at a constant temperature of 80 °C overnight. The colour of the solution changed to blue during heating and blue plate crystals of $Cu(O_3PC_2H_3) \cdot H_2O$ were formed. The crystals were recovered by filtration and washed with distilled water and ethanol, giving the pure product in 90% yield (1.7 g). Anal. calc. for $C_2H_5O_4PCu$ ($M = 186.92$ g mol^{-1}): C, 12.83; H, 2.67%. Found: C, 12.79; H, 2.61%.

Synthesis of $Zn(O_3PC_2H_3) \cdot H_2O$ (II)

$Zn(O_3PC_2H_3) \cdot H_2O$ was prepared by the same method used for **I** above, replacing copper oxide with zinc oxide (0.81 g, 10 mmol). The crystals were recovered in 92% yield (1.75 g). Anal. calc. for $C_2H_5O_4PZn$ ($M = 189.42$ g mol^{-1}): C, 12.67; H, 2.64%. Found: C, 12.65; H, 2.62%.

X-Ray structure analysis

For **I**, data were recorded on a Bruker Smart 6000 diffractometer equipped with a CCD detector system and a copper sealed-tube source. 3636 images of size 0.3° were recorded, each for 20 s. The structure was solved by direct methods using SHELXTL[9] and refined using SHELXL97.[10] The protons of the water molecules were located in the Fourier difference map. The vinyl protons were placed in calculated positions and refined with a riding model.

For **II**, 2251 images of 0.3° were recorded, each for 20 s. The diffractometer and programs used were the same as for **I**. Protons were treated the same way, except for those of the water molecule, which were not located. The high atomic displacement parameters for one carbon [C(2)] of the vinyl group suggest that the group is either disordered on sites in close proximity on either side of the mirror plane or that the group is undergoing large displacements. Attempts to model disorder on two sites across the mirror plane led to the two positions merging and were abandoned.

Crystallographic data and refinement conditions for both **I** and **II** are given in Table 1. Atomic parameters for **I** and **II** are listed in Table 2, with selected bond distances and angles for both structures in Table 3.

CCDC reference numbers 182285 and 182286. See http://www.rsc.org/suppdata/nj/b2/b200438k/ for crystallographic data in CIF or other electronic format.

Discussion

The structure of the copper vinylphosphonate monohydrate (**I**) is layered, as shown in Fig. 1. Within the layer, the copper atom is coordinated by five oxygen atoms (Fig. 2), one of which is from a water molecule [O(4)], as has been observed

Table 1 Crystallographic data for copper vinylphosphonate (**I**) and zinc vinylphosphonate (**II**)

	I	II
Formula	$CuPO_3C_2H_3 \cdot H_2O$	$ZnPO_3C_2H_3 \cdot H_2O$
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1/c$	$Pmn2_1$
a/Å	9.8699(1)	5.6805(1)
b/Å	7.6192(1)	9.8101(1)
c/Å	7.3171(1)	4.7988(1)
β/°	95.803(1)	—
Unit cell volume/Å^3	547.432(12)	267.42(1)
Z	4	2
T/K	296	296
λ/Å	1.54178	1.54178
μ/mm^{-1}	7.854	8.652
Crystal size/mm	$0.20 \times 0.20 \times 0.10$	$0.10 \times 0.08 \times 0.04$
Unique reflections	982	425
R(int) [$I > 2\sigma(I)$]	0.026	0.026
R_1	0.029	0.033
wR_2	0.073	0.086

Table 2 Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for **I** and **II**. U(eq) is defined as one third of the trace of the orthogonalised U_{ij} tensor

	x	y	z	U(eq)
I				
Cu(1)	0.5440(1)	−0.1891(1)	0.630(1)	0.014(1)
P(1)	0.6581(1)	−0.5498(1)	0.1780(1)	0.011(1)
O(1)	0.6509(2)	−0.3984(2)	0.405(2)	0.016(1)
O(2)	0.3811(2)	−0.2754(2)	−0.862(2)	0.019(1)
O(3)	0.4291(2)	−0.85(2)	0.1660(2)	0.016(1)
O(4)	0.7054(2)	−0.654(2)	0.1927(2)	0.020(1)
C(1)	0.8311(3)	−0.5726(4)	0.2718(4)	0.025(1)
C(2)	0.9287(3)	−0.4706(6)	0.2318(6)	0.054(1)
II				
Zn(1)	0	0.5255(1)	0.8308(3)	0.023(1)
P(1)	0	0.3326(1)	1.2778(3)	0.019(1)
O(1)	0	0.3515(5)	1.5931(14)	0.026(1)
O(2)	0.2148(6)	0.3969(3)	1.1327(8)	0.027(1)
O(3)	0	0.6842(5)	1.1375(15)	0.028(1)
C(1)	0	0.1564(7)	1.2020(20)	0.041(2)
C(2)	0	0.0554(12)	1.3760(40)	0.20(17)

Table 3 Bond lengths (Å) and angles (°) for structures **I** and **II**

I		**II**	
Cu(1)–O(1)	1.9288(16)	Zn(1)–O(2)^a	2.027(3)
Cu(1)–O(2)	1.9636(17)	Zn(1)–O(2)^b	2.027(4)
Cu(1)–O(3)	1.9801(16)	Zn(1)–O(1)^c	2.052(5)
Cu(1)–O(4)	2.0052(18)	Zn(1)–O(3)	2.143(6)
Cu(1)–O(3)^d	2.2881(16)	Zn(1)–O(2)	2.275(4)
O(1)–Cu(1)–O(2)	95.75(7)	O(2)^a–Zn(1)–O(2)^b	106.1(2)
O(2)–Cu(1)–O(3)	88.62(7)	O(2)^a–Zn(1)–O(1)^c	92.96(14)
O(1)–Cu(1)–O(4)	90.78(7)	O(2)^a–Zn(1)–O(3)	92.82(16)
O(3)–Cu(1)–O(4)	87.22(7)	O(1)^c–Zn(1)–O(3)	170.4(3)
O(1)–Cu(1)–O(3)^d	112.12(6)	O(2)^a–Zn(1)–O(2)	159.30(17)
O(2)–Cu(1)–O(3)^d	87.84(6)	O(2)^b–Zn(1)–O(2)	94.48(8)
O(3)–Cu(1)–O(3)^d	86.28(6)	O(1)^c–Zn(1)–O(2)	83.87(17)
O(4)–Cu(1)–O(3)^d	83.78(6)	O(3)–Zn(1)–O(2)	88.02(18)
		O(2)–Zn(1)–O(2)^e	64.86(18)

^{a} $x-1/2,-y+1,z-1/2$. ^{b} $-x+1/2,-y+1,z-1/2$. ^{c} $x,y,z-1$. ^{d} $-x+1,-y,-z$. ^{e} $-x,y,z$.

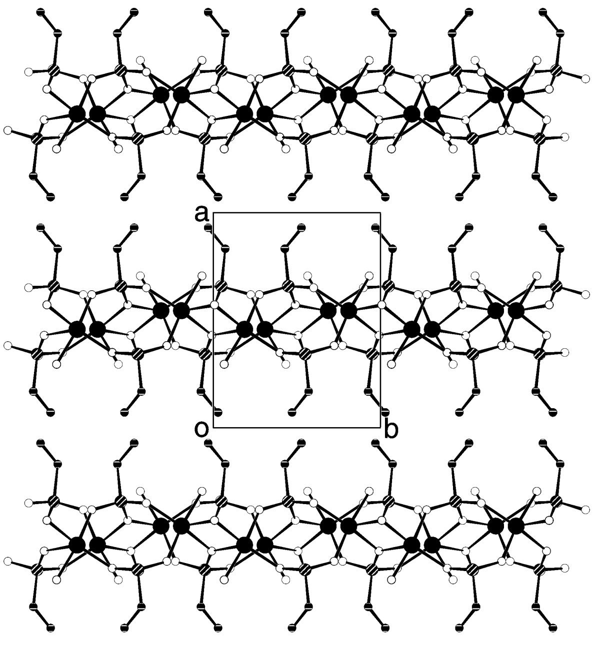

Fig. 1 The crystal structure of $Cu(O_3PC_2H_3){\cdot}H_2O$ (**I**) viewed down the *c*-axis. Hydrogen atoms have been omitted for clarity.

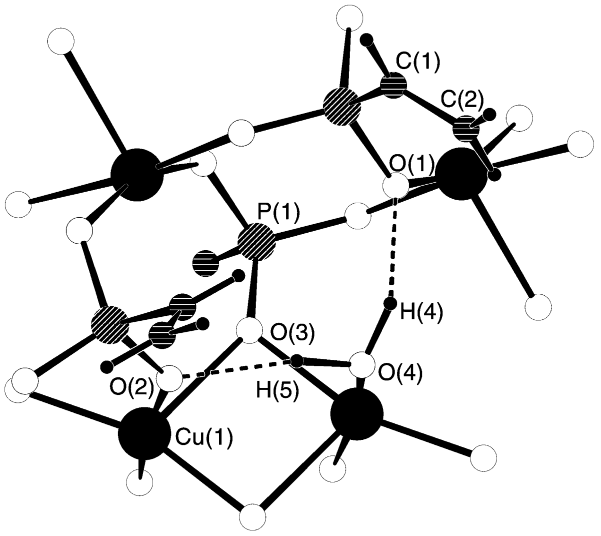

Fig. 2 A segment of the crystal structure of **I**, showing the distorted square pyramidal coordination of the Cu atoms and the hydrogen bonding interactions (dashed lines).

previously in other copper phosphonate structures.[6,7] The coordination sphere is a distorted square pyramid, with O–Cu–O angles in the range 83.78(6)–112.12(6)° and Cu–O bond distances in the range 1.929(2)–2.288(2) Å. The closest contact between copper atoms is 3.122(1) Å for two atoms that are bridged by two oxygen atoms [O(3)] to form a 4-membered ring. In addition to bridging two Cu atoms, O(3) is bonded to the phosphorus atom, with the phosphorus atom tetrahedrally coordinated by three oxygen atoms and one carbon atom of the vinyl group. The water molecule forms hydrogen bonds to two oxygen atoms within the layer, with distances of 2.668(2) Å for O(4)···O(1) and 2.818(2) Å for O(4)···O(2).

The copper phosphonate layers are stacked along the *a*-axis and are related to each other by translation with a layer-to-layer distance of 9.87 Å. No direct bonding occurs between separate layers. The 'surface' of each layer consists of vinyl and water groups, with the vinyl groups protruding further into the interlayer region. This allows for a small interdigitation of the vinyl groups from neighbouring layers, resulting in parallel pairs (one from each layer) of C=C bonds only 4.145(5) Å apart. Such an arrangement has previously been shown to be ideal for solid state [2 + 2] cyclodimerisation to occur between similar pairs of vinyl groups.[11,12]

The structure of zinc vinylphosphonate monohydrate (**II**) is also layered (Fig. 3), but, in contrast to the copper structure, each zinc atom is coordinated to six oxygen atoms in the form of a distorted octahedron, with O–Zn–O angles in the range 64.86(18)–106.1(2)° (Fig. 4). This coordination is also as expected by comparison with other zinc phosphonates for which the structure is already known.[1,2] One of the oxygen atoms [O(3)] is from a water molecule, and Zn–O distances in the range 2.027(3)–2.275(4) Å are observed. The phosphorus atom is tetrahedral in coordination, with the closest Zn···P distance being 2.800(2) Å across the four-membered ring formed where the Zn atom is chelated by two O atoms from the same PO_3 group. The water is located on the surface of the layer in a similar manner to that in **I**. The water oxygen can potentially donate four hydrogen bonds [two to O(2), with O···O distances of 2.984(7) Å, and two to O(1), with distances of 2.870(1) Å], as shown in Fig. 4. Water hydrogen atoms were not located, possibly due to disorder resulting from these competing bonds. O(2) bridges two zinc atoms at a distance of 3.751(1) Å, while potentially accepting a hydrogen bond.

As in the structure of **I**, the layers are related by translation along the *b*-axis with an interlayer distance of *ca.* 9.8 Å. A

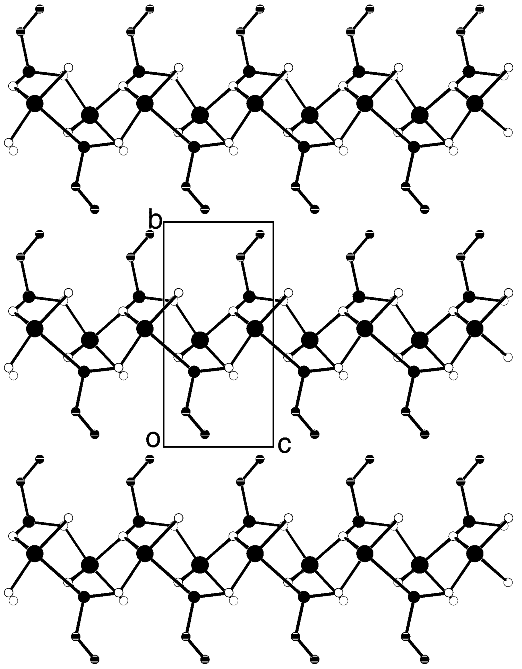

Fig. 3 The crystal structure of $Zn(O_3PC_2H_3)\cdot H_2O$ (**II**) viewed down the *a*-axis. Hydrogen atoms have been omitted for clarity.

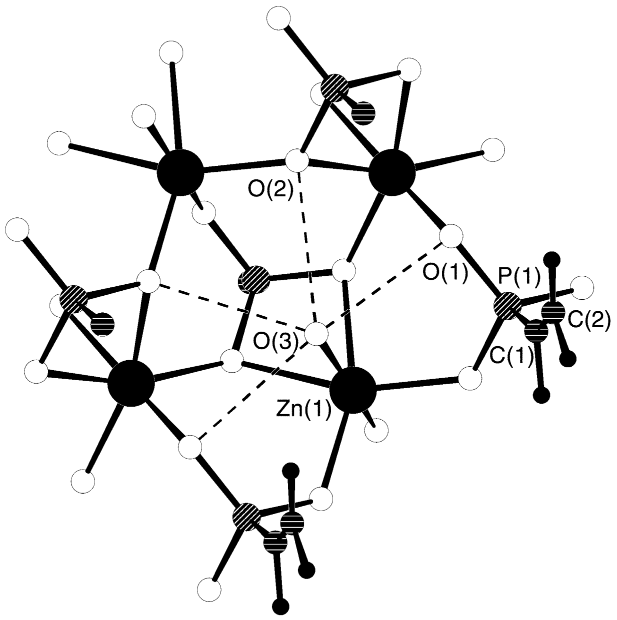

Fig. 4 A segment of the crystal structure of **II**, showing the distorted octahedral coordination of the Zn atoms and the proposed hydrogen bonding interactions between the water molecule and the oxygens of the phosphonate group (dashed lines).

small degree of interdigitation of vinyl groups from adjacent layers occurs, with each vinyl group surrounded by four others from the adjacent layer—the centre-to-centre distance between the double bonds is *ca* 4.3 Å. However, as a consequence of the different coordination of the metal atoms in the layers compared to the copper vinylphosphonate, neighbouring pairs of C=C bonds are not parallel to one another and therefore are not in the ideal orientation for topochemical reaction—the angle between the vinyl groups in the zinc vinylphosphonate is *ca*. 85°.

Conclusion

Through this study, we have shown that metal oxides may be used as precursors to the formation of metal phosphonate materials. Copper vinylphosphonate monohydrate, $Cu(O_3PC_2H_3)\cdot H_2O$, shares structural similarities with other copper phosphonate materials [$Cu(O_3PR)\cdot H_2O$, R = Me, Et or Ph], with the copper atoms in each of these structures adopting a distorted square pyramidal coordination. The structure of zinc vinylphosphonate monohydrate has also been solved from a single crystal X-ray diffraction study, and confirms the expected structure, common amongst the series $M^{II}(O_3PR)\cdot H_2O$ (M = Zn, Mg, Ni, Zn, Co), in which the metal atom is octahedrally coordinated and crystallises in an orthorhombic unit cell.

The close proximity of the vinyl groups within the layers of both copper and zinc vinylphosphonate materials suggests that topochemical reactions in the solid state may be possible. However, due to the different coordination of the metal centres in the two structures the orientation of vinyl groups changes, and we would expect that the parallel alignment of adjacent groups in the copper vinylphosphonate would be significantly more favourable towards reaction than that in the zinc analogue. The near perpendicular alignment in the zinc vinylphosphonate does not, however, preclude the possibility of reaction occurring, especially as the disorder seen within the vinyl groups in this structure may indicate a mechanism for reorientation to occur upon activation. We are currently investigating the topochemical reactions of these vinyl-containing phosphonate materials, as well as a number of other metal phosphonates containing unsaturated organic groups, and will publish our findings at the conclusion of these studies. The presence of vinyl functional groups within the interlayer region of these materials also provides a potential route to the support/immobilisation of catalytic species and investigations into this aspect are also in progress.

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