Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Copper(II) hypophosphite: the α- and β-forms at 270 and 100 K, and the γ-form at 270 K

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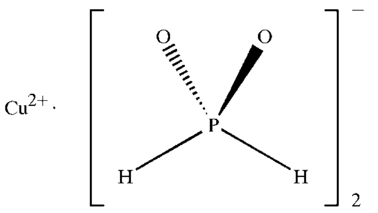
Received 9 January 2002
Accepted 20 March 2002
Online 19 April 2002

Copper(II) hypophosphite has been shown to exist as several polymorphs. The crystal structures of monoclinic α-, orthorhombic β- and orthorhombic γ-$Cu(H_2PO_2)_2$ have been determined at different temperatures. The geometry of the hypophosphite anion in all three polymorphs is very close to the idealized one, with point symmetry *mm*2. Despite having different space groups, the structures of the α- and β-polymorphs are very similar. The polymeric layers formed by the Cu atoms and the hypophosphite ions, which are identical in the α- and β-polymorphs, stack in the third dimension in different ways. Each hypophosphite anion is coordinated to three Cu atoms. On cooling, a minimum amount of contraction was observed in the direction normal to the layers. The structure of the polymeric layers in the γ-polymorph is quite different. There are two symmetry-independent hypophosphite anions; the first is coordinated to two Cu atoms, while the second is coordinated to four Cu atoms. In all three polymorphs, the Cu atoms are coordinated by six O atoms of six hypophosphite anions, forming tetragonal bipyramids; in the α- and β-polymorphs, there are four short and two long Cu—O distances, while in the γ-polymorph, there are four long and two short Cu—O distances.

Comment

The first structural studies of ammonium hypophosphite and hexahydrates of cobalt, nickel and magnesium hypophosphites were reported 65 years ago (Zachariasen & Mooney, 1934; Ferrari & Colla, 1937). The crystal structures of hypophosphites of anhydrous calcium (Wyckoff, 1964), zinc (Tanner *et al.*, 1997), germanium (Weakley, 1983), erbium (Aslanov *et al.*, 1975), uranium (Tanner *et al.*, 1992), and a urea complex of copper (Naumov *et al.*, 2001) are known. No structural data for pure copper(II) hypophosphite, (I), have yet been reported. Since precise data on the structure of copper(II) hypophosphite are very important for understanding the mechanism of the decomposition of this salt, which finds numerous practical applications (Lomovsky & Boldyrev, 1994), we have undertaken its single-crystal X-ray structure determination.



(I)

Copper(II) hypophosphite is very unstable; therefore, low temperatures were required both for crystal growth and data collection. A special device for crystal growth, based on the Oxford Cryosystems Cryostream cooler (Naumov, 2001), allowed us to obtain crystals of quality and dimensions acceptable for single-crystal diffraction analysis. The use of a SMART CCD diffractometer allowed us to decrease the time of data collection to 6 h without loss of crystal quality and to collect data at several different temperatures for the same crystal.

Our studies have shown copper(II) hypophosphite to exist as three polymorphs, which we have called the α-, β- and γ-polymorphs. Crystals of all three polymorphs grew from the same solution simultaneously. The α- and β-polymorphs have the same rhombic plate habit and can be distinguished only by structural analysis. The γ-polymorph grew as needles and could be identified visually. Several powder patterns of copper hypophosphite have been reported (Balema *et al.*, 1988; Brun & Dumail, 1971; Michailow *et al.*, 1980), which are different and unindexed. The calculated powder pattern of the needle crystal of the γ-polymorph is in good agreement with the powder pattern published by Brun & Dumail (1971). The calculated powder pattern of the rhombic plate crystal of the first discovered α-polymorph does not completely describe the known powder pattern (Balema *et al.*, 1988). The method of preparation used in the present study excludes the formation of different substances. We successfully undertook a search for additional phases and found two polymorphs of the rhombic plate crystal. The calculated powder patterns of the rhombic plate crystal of the α- and β-polymorphs are in good agreement with the powder patterns published by Balema *et al.* (1988) and Michailow *et al.* (1980). The crystal structures of the α- and β-polymorphs differ from those previously reported for other anhydrous hypophosphites, such as $Zn(H_2PO_2)_2$ (Tanner *et al.*, 1997) and $Ca(H_2PO_2)_2$ (Wyckoff, 1964). It is worth mentioning that the γ-polymorph is isostructural with zinc hypophosphite.

The geometry of the hypophosphite anion in all three polymorphs is very close to the idealized one, with point symmetry *mm*2. The average geometric parameters of the hypophosphite anion in anhydrous $Cu(H_2PO_2)_2$ [P—O 1.51 (2) Å and O—P—O 118.3 (17)°] are in good agreement

DOI: 10.1107/S0108270102005176

with those of the urea complex of copper hypophosphite [P—O 1.515 (5) Å and O—P—O 117.84 (8)°; Naumov *et al.*, 2001]. Despite having different space groups, the structures of the α- and β-polymorphs are very similar. The coordination of the Cu atoms and of the hypophospite anions in the structures are also identical. Each Cu atom is coordinated by six O atoms of six hypophosphite anions, forming a tetragonal bipyramid [α-polymorph (270 K): four short, 1.9454 (19) (× 2) and 1.987 (2) Å (× 2), and two long, 2.653 (2) Å (× 2); β-polymorph (270 K): four short, 1.9483 (16) (× 2) and 1.9829 (16) Å (× 2), and two long, 2.6496 (17) Å (× 2)]. The short Cu—O bonds do not alter during cooling (Tables 1–4). Each hypophosphite anion is coordinated to three Cu atoms. The geometry of the hypophosphite anions (P—O distances and O—P—O angles) does not change during cooling (Tables 1–4). The hypophosphite anions and Cu cations form polymeric layers in the (100) (Fig. 1) and (001) planes (Fig. 2) for the α- and β-polymorphs, respectively. The copper cations form a distorted square pattern, with equal Cu···Cu distances [4.1131 (1) Å at 270 K and 4.0899 (1) Å at 100 K in the α-polymorph; 4.1141 (1) Å at 270 K and 4.0909 (1) Å at 100 K in the β-polymorph]. The layers, which are identical in the α- and β-polymorphs, are stacked in the third dimension in different ways. In the α-polymorph, they align identically above each other [*AAAA*] (Fig. 3) and in the β-polymorph, they align as [*ABAB*] (Fig. 4), *i.e.* not vertically stacked, and it is this alternate stacking pattern which generates the cell edge doubling in the direction perpendicular to the layers [$2a$ (α-polymorph) $\simeq c$ (β-polymorph)].

The coordination of the Cu atoms and hypophospite anions in the γ-polymorph is quite different to that in the α- and β-polymorphs (Table 5). Each Cu atom is coordinated by six O atoms of six hypophosphite anions, forming a tetragonal

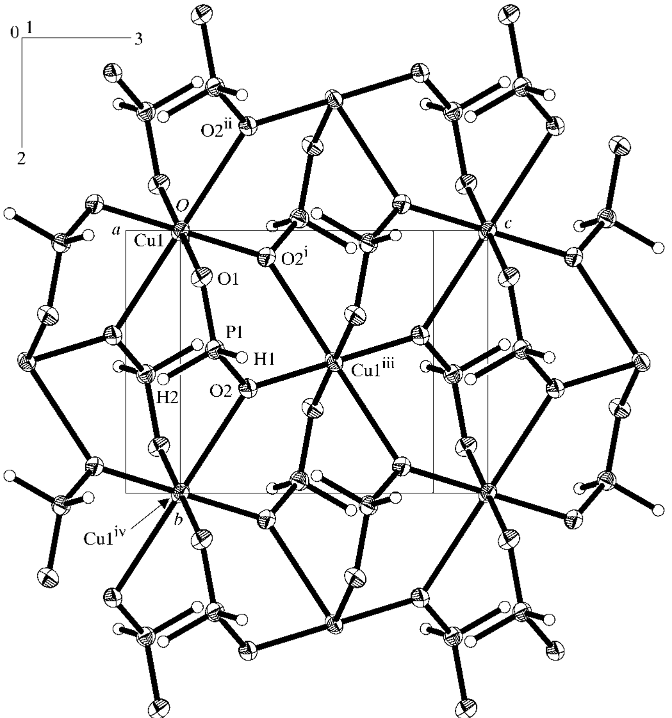


Figure 1
The layer formed by the Cu^{II} cations and hypophosphite anions of the α-polymorph at 270 K, projected on to the (100) plane. Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The crystallographic axes and the axes of the strain tensor on cooling (1 = minimum, 2 = medium and 3 = maximum contraction) are shown.

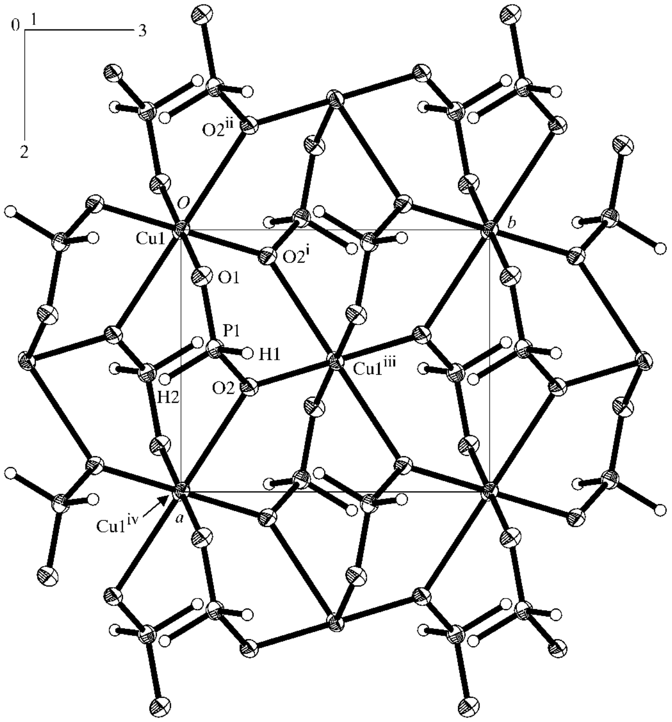


Figure 2
The layer formed by the Cu^{II} cations and hypophosphite anions of the β-polymorph at 270 K, projected on to the (001) plane. Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. The crystallographic axes and the axes of the strain tensor on cooling (1 = minimum, 2 = medium and 3 = maximum contraction) are shown. Axis 1 is normal to the projection plane.

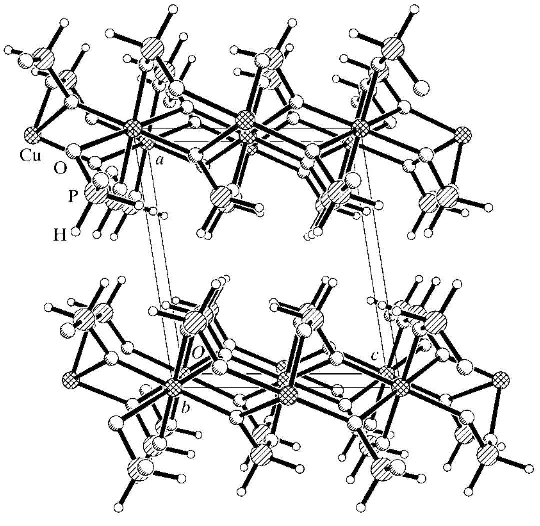


Figure 3
Packing diagram of the α-polymorph viewed along [010].

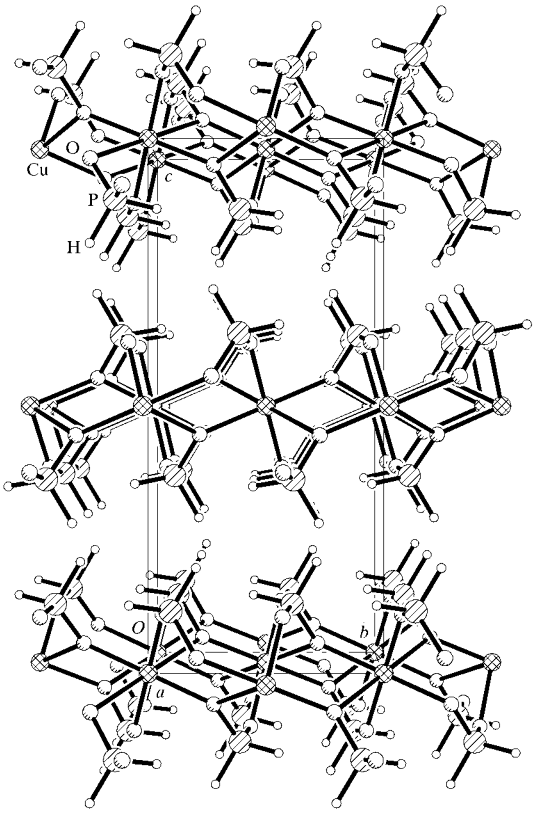


Figure 4
Packing diagram of the β-polymorph viewed along [100].

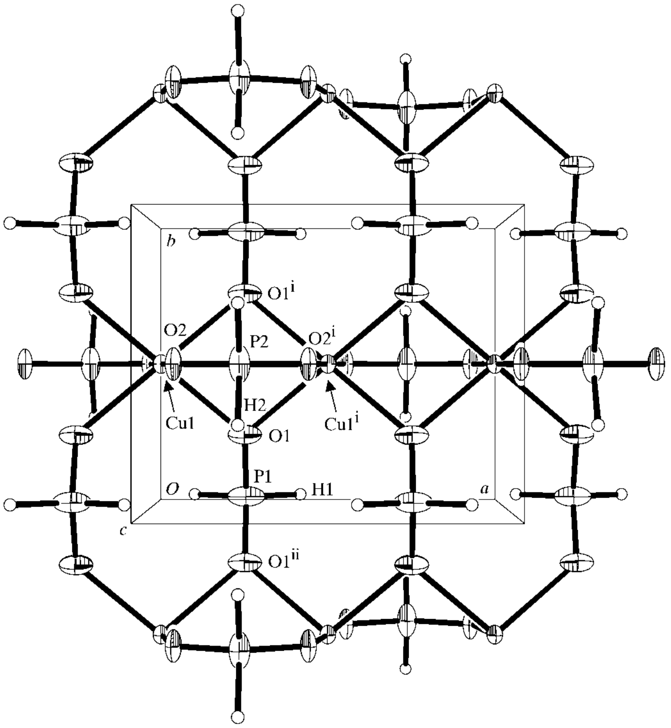


Figure 5
The layer formed by the Cu^{II} cations and hypophosphite anions of the γ-polymorph at 270 K, viewed along [001]. Displacement ellipsoids are plotted at the 50% probability level and H atoms are shown as small spheres of arbitrary radii.

bipyramid [two short, 1.949 (2) Å (× 2), and four long, 2.2046 (14) Å (× 4) at 270 K]. There are two symmetry-independent hypophosphite anions in the structure of the γ-polymorph. The first is coordinated to two Cu atoms, while the second is coordinated to four Cu atoms. The hypophosphite anions and Cu cations form polymeric layers in the (001) planes (Fig. 5). The copper cations form a rectangular pattern, with different Cu$\cdots$Cu distances [3.3369 (3) Å and 5.4133 (5) Å]. The layers are aligned above each other (Fig. 6).

The P and O atoms of the γ-polymorph are rather anisotropic compared with the 270 K data for the α- and β-polymorphs. This can be explained by the existence of vibrational freedom along the [100] and [010] directions of the coordinated hypophosphite anion and less closed packing. The calculated densities are 2.696, 2.699 and 2.472 Mg m^{-3} at 270 K for the α-, β- and γ-polymorphs, respectively.

In all three polymorphs, separate layers are linked by van der Waals interactions. The shortest H$\cdots$H distances between layers are 2.86 (5), 2.55 (4) and 2.67 (3) Å at 270 K for the α-, β- and γ-polymorphs, respectively.

On cooling to 100 K, the structure of the α-polymorph contracted anisotropically. The direction of minimum contraction [0.105 (2)%; axis 1 of the strain tensor in Fig. 1] is close to the normal to the planes of the polymeric layers. The direction of medium contraction [0.460 (4)%; axis 2 of the strain tensor in Fig. 1] coincided with the crystallographic *b* axis. The direction of maximum contraction [0.649 (4)%; axis 3 of the strain tensor in Fig. 1] is close to the crystallographic *c* axis.

On cooling to 100 K, the structure of the β-polymorph contracted anisotropically. The direction of minimum

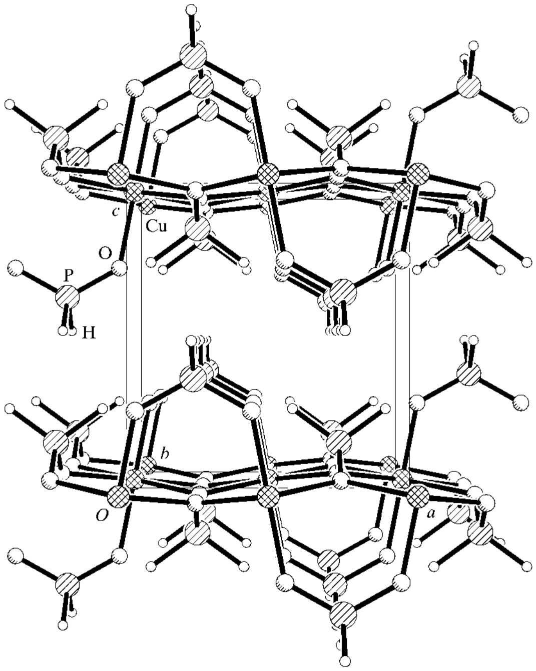


Figure 6
Packing diagram of the γ-polymorph viewed along [010].

contraction [0.114 (4)%; axis 1 of the strain tensor in Fig. 2] coincided with the crystallographic *c* axis and was normal to the planes of the polymeric layers. The direction of medium contraction [0.460 (4)%; axis 2 of the strain tensor in Fig. 2] coincided with the crystallographic *a* axis. The direction of maximum contraction [0.639 (2)%; axis 3 of the strain tensor in Fig. 2] coincided with the crystallographic *b* axis.

The contractions on cooling in the α- and β-polymorphs are very similar. The direction of minimum contraction can be correlated with the repulsive H···H interactions between different layers. The directions of medium and maximum contraction in the layer can be correlated with the contraction of the long Cu1—O2^{ii} distances on cooling [symmetry codes: (ii) $x, y-1, z$, for the α-polymorph; $x-1, y, z$, for the β-polymorph]. On cooling to 100 K, the crystal of the γ-polymorph cracked at about 120 K.

Experimental

Copper(II) hypophosphite was synthesized by adding hypophosphorous acid, H_3PO_2 (2.3771 g of 50% solution in 35 ml of water), to basic copper carbonate, $CuCO_3 \cdot Cu(OH)_2$ (1 g). The reaction mixture was evacuated until carbon dioxide evolution had stopped (about 10 min). Crystals were grown at 278 K from a solution in water under a nitrogen atmosphere. During crystal growth, initial formation of crystals with a rhombic plate habit was observed. The quantity of needle crystals can be increased by adding glycerine and increasing the temperature of the solution to 288 K.

α-Polymorph at 270 K

Crystal data

$Cu(H_2PO_2)_2$
$M_r = 193.51$
Monoclinic, $P2_1/c$
$a = 7.2186\ (1)$ Å
$b = 5.3462\ (2)$ Å
$c = 6.2521\ (3)$ Å
$\beta = 98.8352\ (11)^\circ$
$V = 238.419\ (15)$ Å^3
$Z = 2$
$D_x = 2.696$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 993 reflections
$\theta = 2.9\text{–}29.1^\circ$
$\mu = 5.14$ mm^{-1}
$T = 270\ (2)$ K
Prism, blue
0.19 × 0.11 × 0.03 mm

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: analytical (*XPREP*; Siemens, 1995)
$T_{min} = 0.521$, $T_{max} = 0.859$
1697 measured reflections
620 independent reflections
578 reflections with $I > 2\sigma(I)$
$R_{int} = 0.034$
$\theta_{max} = 29.1^\circ$
$h = -7 \rightarrow 9$
$k = -7 \rightarrow 7$
$l = -8 \rightarrow 8$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.068$
$S = 1.18$
620 reflections
43 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0273P)^2 + 0.2371P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.36$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.033 (5)

Table 1
Selected geometric parameters (Å, °) for the α-polymorph at 270 K.

Cu1—O1	1.9454 (19)	P1—O1	1.516 (2)
Cu1—O2^{i}	1.987 (2)	P1—O2	1.521 (2)
Cu1—O2^{ii}	2.653 (2)		
O1—Cu1—O2^{i}	89.88 (8)	P1—O1—Cu1	130.18 (12)
O1—Cu1—O2^{ii}	91.76 (7)	P1—O2—Cu1^{iii}	122.09 (12)
O2^{i}—Cu1—O2^{ii}	82.78 (5)	P1—O2—Cu1^{iv}	113.66 (10)
O1—P1—O2	118.04 (12)	Cu1^{iii}—O2—Cu1^{iv}	124.25 (9)

Symmetry codes: (i) $-x, y-\frac{1}{2}, \frac{1}{2}-z$; (ii) $x, y-1, z$; (iii) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $x, 1+y, z$.

α-Polymorph at 100 K

Crystal data

$Cu(H_2PO_2)_2$
$M_r = 193.51$
Monoclinic, $P2_1/c$
$a = 7.2079\ (3)$ Å
$b = 5.3216\ (1)$ Å
$c = 6.2121\ (2)$ Å
$\beta = 98.709\ (2)^\circ$
$V = 235.534\ (13)$ Å^3
$Z = 2$
$D_x = 2.729$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1117 reflections
$\theta = 2.9\text{–}29.1^\circ$
$\mu = 5.21$ mm^{-1}
$T = 100\ (2)$ K
Prism, blue
0.19 × 0.11 × 0.03 mm

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: analytical (*XPREP*; Siemens, 1995)
$T_{min} = 0.518$, $T_{max} = 0.857$
1689 measured reflections
612 independent reflections
575 reflections with $I > 2\sigma(I)$
$R_{int} = 0.033$
$\theta_{max} = 29.1^\circ$
$h = -7 \rightarrow 9$
$k = -7 \rightarrow 7$
$l = -8 \rightarrow 8$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.062$
$S = 1.18$
612 reflections
43 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0249P)^2 + 0.3031P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.47$ e Å^{-3}
$\Delta\rho_{min} = -0.42$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.022 (4)

Table 2
Selected geometric parameters (Å, °) for the α-polymorph at 100 K.

Cu1—O1	1.9461 (18)	P1—O1	1.5203 (18)
Cu1—O2^{i}	1.9872 (18)	P1—O2	1.5252 (19)
Cu1—O2^{ii}	2.6213 (18)		
O1—Cu1—O2^{i}	89.94 (7)	P1—O1—Cu1	129.45 (11)
O1—Cu1—O2^{ii}	91.66 (7)	P1—O2—Cu1^{iii}	121.58 (11)
O2^{i}—Cu1—O2^{ii}	83.05 (5)	P1—O2—Cu1^{iv}	113.87 (9)
O1—P1—O2	118.03 (11)	Cu1^{iii}—O2—Cu1^{iv}	124.54 (8)

Symmetry codes: (i) $-x, y-\frac{1}{2}, \frac{1}{2}-z$; (ii) $x, y-1, z$; (iii) $-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iv) $x, 1+y, z$.

β-Polymorph at 270 K

Crystal data

$Cu(H_2PO_2)_2$
$M_r = 193.51$
Orthorhombic, *Pbca*
$a = 5.3259\ (2)$ Å
$b = 6.2720\ (2)$ Å
$c = 14.2590\ (6)$ Å
$V = 476.31\ (3)$ Å^3
$Z = 4$
$D_x = 2.699$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1781 reflections
$\theta = 2.9\text{–}29.1^\circ$
$\mu = 5.15$ mm^{-1}
$T = 270\ (2)$ K
Prism, blue
0.23 × 0.13 × 0.05 mm

Table 3
Selected geometric parameters (Å, °) for the β-polymorph at 270 K.

Cu1—O1	1.9483 (16)	P1—O1	1.5151 (18)
Cu1—O2$^{\rm i}$	1.9829 (16)	P1—O2	1.5207 (17)
Cu1—O2$^{\rm ii}$	2.6496 (17)		
O1—Cu1—O2$^{\rm i}$	90.00 (7)	P1—O1—Cu1	128.95 (10)
O1—Cu1—O2$^{\rm ii}$	91.92 (6)	P1—O2—Cu1$^{\rm iii}$	122.84 (10)
O2$^{\rm i}$—Cu1—O2$^{\rm ii}$	82.10 (4)	P1—O2—Cu1$^{\rm iv}$	112.51 (8)
O1—P1—O2	118.31 (10)	Cu1$^{\rm iii}$—O2—Cu1$^{\rm iv}$	124.64 (7)

Symmetry codes: (i) $x-\frac{1}{2},\frac{1}{2}-y,-z$; (ii) $x-1,y,z$; (iii) $\frac{1}{2}+x,\frac{1}{2}-y,-z$; (iv) $1+x,y,z$.

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: analytical (*XPREP*; Siemens, 1995)
$T_{\rm min} = 0.420$, $T_{\rm max} = 0.811$
3218 measured reflections
631 independent reflections
567 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.029$
$\theta_{\rm max} = 29.1°$
$h = -7 \rightarrow 7$
$k = -7 \rightarrow 8$
$l = -17 \rightarrow 19$
Intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.024$
$wR(F^2) = 0.059$
$S = 1.27$
631 reflections
43 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0226P)^2 + 0.5274P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.62$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.30$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0090 (16)

β-Polymorph at 100 K

Crystal data

Cu(H$_2$PO$_2$)$_2$
$M_r = 193.51$
Orthorhombic, *Pbca*
$a = 5.3014$ (2) Å
$b = 6.2319$ (2) Å
$c = 14.2427$ (2) Å
$V = 470.55$ (2) Å^3
$Z = 4$
$D_x = 2.732$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1900 reflections
$\theta = 2.9$–$29.1°$
$\mu = 5.21$ mm^{-1}
$T = 100$ (2) K
Prism, blue
0.23 × 0.13 × 0.05 mm

Data collection

Siemens SMART CCD diffractometer
ω scans
Absorption correction: analytical (*XPREP*; Siemens, 1995)
$T_{\rm min} = 0.417$, $T_{\rm max} = 0.809$
2974 measured reflections
624 independent reflections
606 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.029$
$\theta_{\rm max} = 29.1°$
$h = -7 \rightarrow 7$
$k = -7 \rightarrow 8$
$l = -17 \rightarrow 19$
Intensity decay: none

Table 4
Selected geometric parameters (Å, °) for the β-polymorph at 100 K.

Cu1—O1	1.9526 (18)	P1—O1	1.5209 (19)
Cu1—O2$^{\rm i}$	1.9835 (18)	P1—O2	1.5247 (19)
Cu1—O2$^{\rm ii}$	2.6178 (18)		
O1—Cu1—O2$^{\rm i}$	90.03 (7)	P1—O1—Cu1	127.87 (11)
O1—Cu1—O2$^{\rm ii}$	91.89 (7)	P1—O2—Cu1$^{\rm iii}$	122.32 (11)
O2$^{\rm i}$—Cu1—O2$^{\rm ii}$	82.25 (5)	P1—O2—Cu1$^{\rm iv}$	112.70 (9)
O1—P1—O2	118.31 (10)	Cu1$^{\rm iii}$—O2—Cu1$^{\rm iv}$	124.94 (8)

Symmetry codes: (i) $x-\frac{1}{2},\frac{1}{2}-y,-z$; (ii) $x-1,y,z$; (iii) $\frac{1}{2}+x,\frac{1}{2}-y,-z$; (iv) $1+x,y,z$.

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.028$
$wR(F^2) = 0.062$
$S = 1.29$
624 reflections
43 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0198P)^2 + 1.1490P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.68$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.33$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.0101 (17)

γ-Polymorph at 270 K

Crystal data

Cu(H$_2$PO$_2$)$_2$
$M_r = 193.51$
Orthorhombic, *Pmma*
$a = 6.6738$ (6) Å
$b = 5.4133$ (5) Å
$c = 7.1954$ (6) Å
$V = 259.95$ (4) Å^3
$Z = 2$
$D_x = 2.472$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 24 reflections
$\theta = 10$–$15°$
$\mu = 4.72$ mm^{-1}
$T = 270$ (2) K
Needle, blue
0.52 × 0.03 × 0.01 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$2\theta/\theta$ scans
Absorption correction: analytical (*XPREP*; Siemens, 1995)
$T_{\rm min} = 0.501$, $T_{\rm max} = 0.605$
939 measured reflections
405 independent reflections
341 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.042$
$\theta_{\rm max} = 29.1°$
$h = -1 \rightarrow 8$
$k = -1 \rightarrow 7$
$l = -1 \rightarrow 9$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.033$
$wR(F^2) = 0.045$
$S = 1.10$
405 reflections
27 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2)]$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.42$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.51$ e Å^{-3}

Table 5
Selected geometric parameters (Å, °) for the γ-polymorph at 270 K.

Cu1—O1	2.2046 (14)	P1—O1	1.518 (2)
Cu1—O2	1.949 (2)	P2—O2	1.485 (2)
O1—Cu1—O1$^{\rm i}$	80.01 (9)	O2—P2—O2$^{\rm i}$	121.4 (2)
O2—Cu1—O1	88.33 (8)	P1—O1—Cu1	127.47 (6)
O2—Cu1—O1$^{\rm i}$	88.33 (8)	P2—O2—Cu1	130.37 (15)
O1—P1—O1$^{\rm ii}$	116.3 (2)	Cu1—O1—Cu1$^{\rm i}$	98.36 (9)

Symmetry codes: (i) $\frac{1}{2}-x,1-y,z$; (ii) $\frac{1}{2}-x,-y,z$.

In all three structures, the H atoms were located from a difference electron-density map. The positions of the H atoms in the α- and β-polymorphs were refined without constraints. The positions of H atoms in γ-polymorph were refined as CH$_2$ groups with fixed O—P—H angles and free P—H bond lengths.

For the α- and β-polymorphs, data collection: *SMART* (Siemens, 1994); cell refinement: *SAINT* (Siemens, 1994); data reduction: *SAINT*. For the γ-polymorph, data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *CAD*-4 *Software*. For all polymorphs, program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1994); software used to prepare material for publication: *SHELXL*97.

The present experimental study was carried out at the University of Durham. Financial support (for DYN) from the Royal Society, London, is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV1101). Services for accessing these data are described at the back of the journal.

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