Redetermination of copper(II) hydrogenphosphite dihydrate

Brahim El Bali[a] and Werner Massa[b]*

[a]Laboratoire des Matériaux et Protection de l'Environnement, Département de Chimie, Faculté des Sciences Dhar Mehraz, BP 1796 Atlas 30003, Fès, Morocco, and [b]Fachbereich Chemie, Philipps-Universität, 35032 Marburg, Germany

Correspondence e-mail: massa@chemie.uni-marburg.de

Key indicators

Single-crystal X-ray study

T = 193 K

Mean σ(P–O) = 0.001 Å

R factor = 0.022

wR factor = 0.047

Data-to-parameter ratio = 21.4

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

The structure of copper(II) hydrogenphosphite dihydrate, $CuHPO_3 \cdot 2H_2O$, has been redetermined on the basis of area-detector data. The results confirm the literature data of Handlovič [*Acta Cryst.* (1969), B**25**, 227–231] but with s.u. values about ten times lower and with all H-atom positions located. The microporous framework topology of the structure is discussed.

Comment

In the course of attempts to prepare phosphites of Cu[I], crystals of the Cu[II] hydrogenphosphite dihydrate, $CuHPO_3 \cdot 2H_2O$, were obtained together with metallic copper, obviously in a disproportionation reaction. This compound is interesting because of the Jahn–Teller distortion of the Cu coordination and its microporous polymeric structure. As the only structural information in the literature is based on film data (Handlovič, 1965, 1969), we reinvestigated the structure by means of an image-plate diffractometer.

The results confirm Handlovič's structure, but the s.u. values are reduced by a factor of ten. The structure shows chains of square pyramidal $[CuO_3(H_2O)_2]$ units, linked by bidentate hydrogenphosphite anions (Fig. 1). In addition, the Cu coordination is completed to strongly elongated octahedral by a weak contact [3.000 (1) Å] to the O5 aqua ligand of a neighbouring pyramid. Fig. 2 shows the additional linking of these chains by the third O atom of the hydrogenphosphite anions to form a three-dimensional network. The changes in bond lengths as compared with Handlovič's results are up to 0.035 Å and result in a more uniform geometry. The P—O bond lengths in the hydrogenphosphite anion are now 1.531–1.536 (1) Å instead of 1.498–1.516 (12) Å. The Cu—O distances to the three hydrogenphosphite ligands are 1.949 (1)–1.953 (1) Å instead of 1.952 (12)–1.977 (11) Å. All H atoms could now be located and refined with isotropic
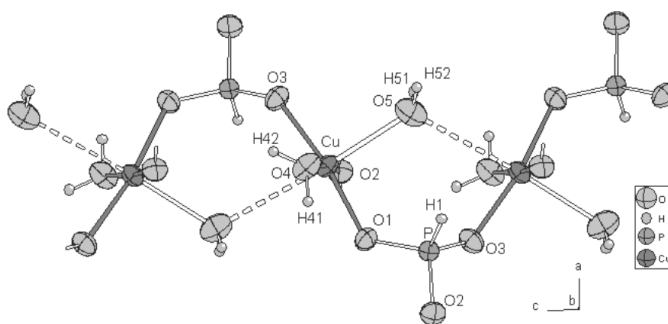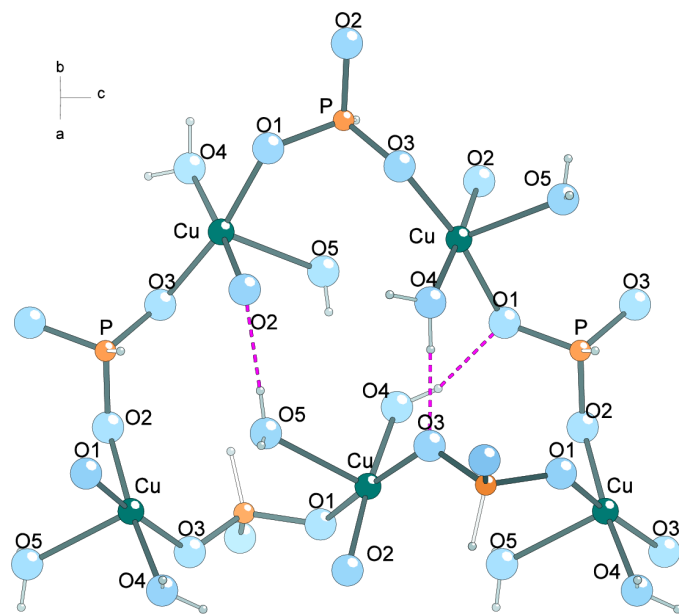

Figure 1

The chain element in $CuHPO_3 \cdot 2H_2O$. Displacement ellipsoids are at the 90% probability level.
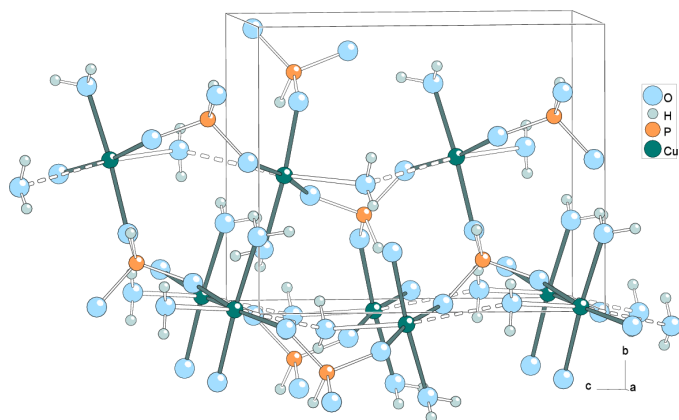
Figure 2
The interconnection of three chains *via* HPO_3^{2-} anions.

displacement parameters. The hydrogenphosphite group is approximately tetrahedral [angles 107.8 (1)–111.91 (6)°]. The H1 atom at phosphorus is not involved in a hydrogen bond. From the equatorial O4 aqua ligand, two hydrogen bonds are formed towards two neighbouring chains [O4···O1 2.629 (2) Å and O4···O3 2.721 (2) Å], from the axial O5 aqua ligand, only one [O5···O2 2.629 (2) Å].

The compound is isostructural with the Cr^{II} compound $CrHPO_3·2H_2O$ (Brynda *et al.*, 1987), which is subject to a similar Jahn–Teller distortion owing to its d^4 configuration. In the paper of Brynda *et al.*, a closer discussion of the structure is given. In addition, it seems remarkable that the three-dimensional network may be described by interconnected large-sized 20-membered rings formed by alternating five Cu octahedra and five hydrogenphosphite tetrahedra. The above-mentioned hydrogen bonds point across these micropores (Fig. 3).

Figure 3
The 20-membered ring element with hydrogen bonds.

Experimental

Crystals were prepared by adding 20 ml of a 0.1 *M* solution of Cu_2O, dissolved in HCl, to 25 ml of 1 *M* H_3PO_3. The resulting blue mixture was stirred for 8 h at 333 K; after cooling, it was left at room temperature. After a few days, large blue blocks were deposited together with a red–brown powder identified as metallic Cu. The blue crystals were isolated and washed with 80% ethanol.

Crystal data

$CuHPO_3·2H_2O$	Mo $K\alpha$ radiation
$M_r = 179.55$	Cell parameters from 8000
Orthorhombic, $P2_12_12_1$	reflections
$a = 6.6906 (5)$ Å	$\theta = 3.6$–$32.8°$
$b = 7.3727 (5)$ Å	$\mu = 5.21$ mm^{-1}
$c = 8.9552 (5)$ Å	$T = 193 (2)$ K
$V = 441.74 (5)$ Å^3	Block, light blue
$Z = 4$	$0.08 \times 0.06 \times 0.05$ mm
$D_x = 2.700$ Mg m^{-3}	

Data collection

Stoe IPDS-II image-plate	1798 independent reflections
diffractometer	1765 reflections with $I > 2\sigma(I)$
ω scans with 1° frames	$R_{int} = 0.087$
Absorption correction: multi-scan	$\theta_{max} = 34.0°$
(*SHELXTL*; Sheldrick, 1996)	$h = -10 \rightarrow 10$
$T_{min} = 0.406$, $T_{max} = 0.710$	$k = -11 \rightarrow 11$
11632 measured reflections	$l = -14 \rightarrow 14$

Refinement

Refinement on F^2	$(\Delta/\sigma)_{max} < 0.001$
$R[F^2 > 2\sigma(F^2)] = 0.022$	$\Delta\rho_{max} = 0.66$ e Å^{-3}
$wR(F^2) = 0.047$	$\Delta\rho_{min} = -0.62$ e Å^{-3}
$S = 1.10$	Extinction correction: *SHELXL*
1798 reflections	Extinction coefficient: 0.019 (3)
84 parameters	Absolute structure: Flack (1983);
All H-atom parameters refined	1928 Friedel pairs
$w = 1/[\sigma^2(F_o^2) + (0.02P)^2$	Flack parameter = 0.010 (8)
$+ 0.05P]$	
where $P = (F_o^2 + 2F_c^2)/3$	

Table 1
Selected geometric parameters (Å, °).

Cu—O2	1.9488 (10)	P—O1	1.5349 (11)
Cu—O1^i	1.9499 (11)	P—O3	1.5364 (11)
Cu—O3^{ii}	1.9531 (10)	P—H1	1.19 (2)
Cu—O4	1.9822 (12)	O4—H41	0.91 (3)
Cu—O5	2.3168 (12)	O4—H42	0.86 (4)
Cu—O5^{iii}	3.0001 (13)	O5—H51	0.80 (3)
P—O2	1.5310 (12)	O5—H52	0.82 (3)
O2—Cu—O1^i	92.95 (5)	O2—P—O1	108.52 (6)
O2—Cu—O3^{ii}	93.17 (5)	O2—P—O3	111.12 (6)
O1^i—Cu—O3^{ii}	170.12 (4)	O1—P—O3	111.91 (6)
O2—Cu—O4	173.88 (5)	O2—P—H1	107.8 (12)
O1^i—Cu—O4	85.61 (5)	O1—P—H1	109.1 (12)
O3^{ii}—Cu—O4	87.49 (5)	O3—P—H1	108.3 (12)
O2—Cu—O5	89.65 (5)	P—O1—Cu^{iv}	130.13 (7)
O1^i—Cu—O5	93.14 (5)	P—O2—Cu	126.93 (7)
O3^{ii}—Cu—O5	94.65 (5)	P—O3—Cu^v	127.11 (7)
O4—Cu—O5	96.36 (5)	Cu—O4—H41	114 (2)
O2—Cu—O5^{iii}	84.08 (4)	Cu—O4—H42	117 (2)
O1^i—Cu—O5^{iii}	91.36 (4)	H41—O4—H42	106 (3)
O3^{ii}—Cu—O5^{iii}	81.57 (4)	Cu—O5—H51	108 (2)
O4—Cu—O5^{iii}	90.01 (4)	Cu—O5—H52	125 (2)
O5—Cu—O5^{iii}	172.461 (11)	H51—O5—H52	100 (3)

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

Data collection: *XAREA* (Stoe & Cie, 2001); cell refinement: *XAREA*; data reduction: *XAREA*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *DIAMOND* (Brandenburg, 1999).

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