Table 6. *Intermolecular distances less than* 3·5 Å

| | | | |
|---|---|---|---|
| O(1)–C($8^{i}$) | 3·317 (4) | C(14)–N($2^{ii}$) | 3·471 (7) |
| N(1)–N($2^{ii}$) | 2·972 (4) | O(2)–C($9^{iii}$) | 3·396 (5) |
| H(1)–N($2^{ii}$) | 2·11 (4) | C(6)–O($1^{iv}$) | 3·347 (5) |

Symmetry code

(i) $1 + x, \quad y, \quad 1 + z$ (iii) $-x, \quad -y, \quad 1 - z$
(ii) $1 + x, \quad y, \quad z$ (iv) $-\frac{1}{2} + x, \quad \frac{1}{2} - y, \quad -1 + z$

are slightly below this plane. Both acetyl groups are directed counter to one another showing that there is no symmetry element in the molecule. Practically the same C=O bond lengths are observed for both carbonyl groups. The $\beta$-pyridyl ring is attached to C(3) in a pseudo-axial position and lies in a plane perpendicular to the mean plane of the 1,4-dihydropyridine ring. The calculation of the intermolecular distances (Table 6) reveals the possible existence of a hydrogen bond between the N(1) and N($2^{ii}$) atoms belonging to neighbouring molecules: H(1)$\cdots$N($2^{ii}$) is 2·11 (4) Å and N(1)–H(1)$\cdots$N($2^{ii}$) is 175 (3)°. In this way the molecules form parallel straight chains along the $x$ axis of the asymmetric unit, the bonded molecules having the same symmetry operation with an $x$ translation.

The authors express their thanks to Professor Dr P. Nantka-Namirski for kindly supplying the sample and for valuable discussion.

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# Copper(II) Phosphate

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**Abstract.** Triclinic, $P\bar{1}$, $a = 4{\cdot}8537$ (7), $b = 5{\cdot}2855$ (6), $c = 6{\cdot}1821$ (8) Å, $\alpha = 72{\cdot}35$ (1), $\beta = 86{\cdot}99$ (1), $\gamma = 68{\cdot}54$ (1)°, $Cu_3(PO_4)_2$, $Z = 1$, $D_x = 4{\cdot}503$ g cm$^{-3}$, isostructural with stranskiite. Crystals were grown hydrothermally from 0·1 $M$ $H_3PO_4$ at 450 °C at 40 000 p.s.i.

**Introduction.** As part of a continuing study of the crystal chemistry of basic phosphates of the divalent Cu ion (Anderson, Shoemaker, Kostiner & Ruszala, 1977; Shoemaker, Anderson & Kostiner, 1977) we have grown single crystals of anhydrous $Cu_3(PO_4)_2$ and determined its crystal structure.

Hanawalt, Rinn & Frevel (1938) reported the X-ray powder diffraction pattern of a 'fused salt', $Cu_3(PO_4)_2$, which was positively identified by Royen & Brenneis (1963). Although $Cu_3(PO_4)_2$ often appears in the literature as the assumed precipitation product of low-temperature neutralization reactions, these reactions generally result in a highly hydrated amorphous mixture or a crystalline hydroxyphosphate [*e.g.* libethenite, $Cu_2(PO_4)OH$]. Crystals of $Cu_3(PO_4)_2$ of a size suitable for single-crystal X-ray diffraction have apparently not been produced and identified until this time.

A blue powder containing predominantly $Cu_3(PO_4)_2$ was produced by repeated sintering of $(NH_4)_2HPO_4$ and CuO at 1000 °C for 5 d. This powder was welded into a gold capsule with 0·1 $M$ $H_3PO_4$ solution in the ratio of 0·1 g powder to 0·4 ml solution, placed into a cold-seal hydrothermal bomb and heated under hydrostatic pressure to 450 °C. Crystals of $Cu_3(PO_4)_2$ up to 0·4 mm in size have been produced after 5 d at 32 000–45 000 p.s.i.

Precession photographs revealed triclinic symmetry. Subsequent analysis showed the space group to be $P\bar{1}$, in which the final refinements were carried out.

Attempts to grind a crystal into a spherical shape were foiled by a well-developed cleavage. Data were therefore collected on a small euhedral crystal with dimensions 0·11 × 0·08 × 0·08 mm ($V = 0{\cdot}97 \times 10^{-3}$ cm$^3$). Three pairs of well-developed faces were found to be normal to major reciprocal lattice rows as judged by precession, rotating crystal and Weissenberg photographs. To simplify absorption corrections, these faces were indexed as (100), (010) and (001) and intensity data were collected on the basis of this arbitrary unit cell.

The lattice parameters were determined in a *PICK*-II least-squares refinement program, with 40 reflections within the angular range $55° < 2\theta < 60°$, each automatically centered on a Picker FACS-I four-circle diffractometer using Mo $K\alpha_1$ radiation ($\lambda = 0{\cdot}70930$ Å).

Diffraction intensities were measured with Zr-filtered Mo $K\alpha$ radiation at a take-off angle of 3·0° with the diffractometer operating in the $\omega$-scan mode. 10 s background counts were taken at both ends of a 1·4° $\theta$–$2\theta$ scan corrected for dispersion. Of the 1368 independent data investigated in the angular range $2\theta <$ 71°, 1240 were considered observable according to the criterion $|F_o| > 3{\cdot}0\sigma_F$, where $\sigma_F$ is defined as $0{\cdot}021|F_o| + [C + k^2B]^{1/2}/2|F_o|\mathrm{Lp}$; the total scan count is $C$, $k$ is the ratio of scanning time to the total background time, and $B$ is the total background count. Three reflections were systematically monitored; the maximum variation in intensity observed was never greater than ±3% over the data collection period. Intensity data were corrected for Lorentz and polarization effects, and absorption corrections ($\mu = 122$ cm$^{-1}$, Mo $K\alpha$) were made with a program written by N. W. Alcock and B. Lee for a crystal of general shape. The maximum absorption correction was 16% of $|F_o|$.

The atomic positions were determined with Patterson and Fourier techniques. Full-matrix least-squares refinement (Busing, Martin & Levy, 1962) with these positional parameters, a $1/\sigma^2$ weighting scheme, zero-valent scattering factors for Cu, P and O (*International Tables for X-ray Crystallography*, 1974), isotropic temperature factors, and corrections for secondary extinction and anomalous dispersion, yielded a residual $R = 0{\cdot}054$ and a weighted residual $R_w = 0{\cdot}075$. The final anisotropic refinement, based on a data:parameter ratio of 20 with 62 independently varied parameters, yielded $R = 0{\cdot}038$ and $R_w = 0{\cdot}056$ for the observed data. The maximum extinction correction (Zachariasen, 1968) was 26% of $|F_o|$ for the $0\bar{1}\bar{2}$ reflection.

A Delauney reduction of the cell parameters of the data collection (morphological) cell showed that it was not the reduced unit cell. The old $c$ axis is actually a body diagonal $[\bar{1}1\bar{1}]$ of the proper reduced cell which is given with $abc;\alpha, \beta, \gamma < 90°$C (after Buerger, 1956; Type 1, triacute). The cell metrics for the reduced cell as refined by *PICK*-II are $a = 4{\cdot}8537\,(7)$, $b = 5{\cdot}2855\,(6)$, $c = 6{\cdot}1821\,(8)$ Å, $\alpha = 72{\cdot}35\,(1)$, $\beta = 86{\cdot}99\,(1)$, and $\gamma = 68{\cdot}54\,(1)°$. Both the final data set* and the final positional and anisotropic thermal parameters in Table 1 are listed on the basis of the reduced unit cell.

**Discussion.** Early in our investigation of $Cu_3(PO_4)_2$ we suspected (on the basis of similarities in the space group and unit-cell volume) that it might be isostructural with the mineral stranskiite, $Zn_2Cu(AsO_4)_2$, as reported by Plieth & Sanger (1967) and later refined by Calvo & Leung (1969). This is indeed the case. Conversion of the atomic positional parameters of stranskiite (as refined by Calvo & Leung) shows a close agreement with those of $Cu_3(PO_4)_2$.

In $Cu_3(PO_4)_2$ the Cu(1) atom (on an inversion center) is surrounded by two O atoms at 1·924 Å and two at 1·982 Å forming a slightly distorted square-planar coordination (the next nearest O atoms are at 2·95 Å). Cu(2) lies in an irregular polyhedron of five O atoms: four at an average distance of 1·965 Å and a fifth at 2·265 Å giving an average for five-coordination of 2·025 Å (the next nearest O is at 3·06 Å). The phosphate tetrahedron is distorted with an average P—O bond length of 1·546 Å (−0·033, +0·026 Å) and O—P—O angle of 109·4° (−4·8, +2·1°). Bond angles and distances for the cation polyhedra are presented in Table 2. The standard deviations for all bond lengths and angles were computed by the function and error

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32731 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 1. *Fractional atomic coordinates* (× 10$^4$) *and anisotropic thermal parameters for* $Cu_3(PO_4)_2$

Numbers in parentheses are estimated standard deviations in the last significant figure. The $B$'s are defined by the general temperature factor $\exp[-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

| | $x$ | $y$ | $z$ | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Cu(1) | 0 | 0 | 0 | 0·81 (2) | 0·94 (2) | 1·31 (2) | −0·36 (2) | −0·15 (2) | −0·22 (2) |
| Cu(2) | 2776 (1) | 2258 (1) | 3157 (1) | 0·97 (2) | 1·28 (2) | 0·97 (2) | −0·14 (1) | −0·12 (1) | −0·47 (1) |
| P | 3586 (2) | 3534 (2) | 7785 (2) | 0·69 (3) | 0·87 (3) | 0·89 (3) | −0·27 (2) | −0·06 (2) | −0·26 (2) |
| O(1) | −1536 (6) | 3443 (6) | 3389 (5) | 0·95 (9) | 1·06 (9) | 1·16 (9) | −0·24 (7) | −0·08 (7) | −0·14 (7) |
| O(2) | 3324 (6) | 6515 (6) | 1695 (5) | 0·90 (9) | 1·13 (9) | 1·36 (9) | −0·45 (7) | −0·03 (7) | −0·38 (7) |
| O(3) | 2303 (6) | 2274 (6) | 49 (5) | 0·99 (9) | 1·16 (9) | 0·92 (9) | −0·42 (7) | 0·11 (7) | −0·48 (7) |
| O(4) | 3786 (6) | 1498 (6) | 6334 (5) | 1·02 (9) | 1·01 (9) | 0·99 (9) | −0·17 (7) | −0·19 (7) | −0·49 (7) |

Table 2. *Bond distances* (Å), *bond angles* (°), *and polyhedral edge lengths* (Å) *for cation polyhedra*

| | Bond distance[a] | Bond angle[b] | Edge length[c] |
|---|---|---|---|
| (i) Cu(1) polyhedron | | | |
| Cu(1)–O(3) | 2× 1·924 | | |
| Cu(1)–O(2) | 2× 1·982 | | |
| O(2)–Cu(1)–O(3) | | 2× 89·9 | 2·760 |
| O(3)–Cu(1)–O(2) | | 2× 90·1 | 2·765 |
| (ii) Cu(2) polyhedron | | | |
| Cu(2)–O(4) | 1·934 | | |
| Cu(2)–O(3) | 1·944 | | |
| Cu(2)–O(1) | 1·964 | | |
| Cu(2)–O(4′) | 2·019 | | |
| Cu(2)–O(2) | 2·265 | | |
| O(4)–Cu(2)–O(3) | | 168·9 | 3·859 |
| O(4)–Cu(2)–O(1) | | 96·5 | 2·909 |
| O(4)–Cu(2)–O(4′) | | 81·3 | 2·575 |
| O(4)–Cu(2)–O(2) | | 99·6 | 3·213 |
| O(3)–Cu(2)–O(1) | | 90·1 | 2·765 |
| O(3)–Cu(2)–O(4′) | | 87·8 | 2·748 |
| O(3)–Cu(2)–O(2) | | 87·7 | 2·925 |
| O(1)–Cu(2)–O(4′) | | 135·7 | 3·689 |
| O(1)–Cu(2)–O(2) | | 101·8 | 3·296 |
| O(4′)–Cu(2)–O(2) | | 122·3 | 3·754 |
| (iii) P tetrahedron | | | |
| P–O(1) | 1·510 | | |
| P–O(2) | 1·539 | | |
| P–O(3) | 1·561 | | |
| P–O(4) | 1·572 | | |
| O(1)–P–O(2) | | 110·0 | 2·497 |
| O(1)–P–O(3) | | 110·0 | 2·516 |
| O(1)–P–O(4) | | 111·5 | 2·548 |
| O(2)–P–O(3) | | 109·5 | 2·532 |
| O(2)–P–O(4) | | 111·1 | 2·567 |
| O(3)–P–O(4) | | 104·6 | 2·478 |

(*a*) E.s.d.'s: *M*–O 0·003 Å.
(*b*) E.s.d.'s : O–Cu–O angles 0·1 Å; O–P–O angles 0·2 Å.
(*c*) E.s.d.'s O–O distances 0·004 Å.

program (*ORFFE*) of Busing, Martin & Levy (1964). The coordination about the O atoms is unbalanced: O(1) has two neighbors, O(2) and O(3) have three and O(4) has four. The shortest P–O bond (1·510 Å) is to O(1) which is underbonded while the longest (1·572 Å) is to O(4). The anion environments are summarized in Table 3.

The Cu atoms all lie near the (10$\bar{1}$) plane with P atoms lying approximately halfway between the planes and bonding them together. Within the plane of Cu atoms the Cu polyhedra form a continuous network as illustrated in Fig. 1. The Cu(2) polyhedra occur in pairs, sharing an O(4)–O(4′) edge across an inversion center. An edge-sharing pair of Cu(2) polyhedra shares four vertices [two O(2) and two O(3) atoms] with adjacent Cu(1) polyhedra in the same layer. Phosphate tetrahedra also join at these vertices to extend the linkages to adjacent layers. The remaining vertices of the Cu(2)–Cu(2) dimer, O(4) and O(1), corner share only with $PO_4$ tetrahedra.

Table 3. *Bond distances* (Å) *and angles* (°) *for the oxygen polyhedra*

Numbers in parentheses are the e.s.d.'s in the last reported figures.

| | | | |
|---|---|---|---|
| (i) O(1) polyhedron | | | |
| O(1)–P | 1·510 (3) | P–O(1)–Cu(2) | 121·2 (2) |
| O(1)–Cu(2) | 1·964 (3) | | |
| (ii) O(2) polyhedron | | | |
| O(2)–P | 1·539 (3) | P–O(2)–Cu(1) | 123·9 (2) |
| O(2)–Cu(1) | 1·982 (3) | P–O(2)–Cu(2) | 114·4 (2) |
| O(2)–Cu(2) | 2·265 (3) | Cu(1)–O(2)–Cu(2) | 121·7 (1) |
| (iii) O(3) polyhedron | | | |
| O(3)–P | 1·561 (3) | P–O(3)–Cu(1) | 118·1 (2) |
| O(3)–Cu(1) | 1·924 (3) | P–O(3)–Cu(2) | 132·7 (2) |
| O(3)–Cu(2) | 1·944 (3) | Cu(1)–O(3)–Cu(2) | 109·0 (2) |
| (iv) O(4) polyhedron | | | |
| O(4)–P | 1·572 (3) | P–O(4)–Cu(2) | 132·0 (2) |
| O(4)–Cu(2) | 1·934 (3) | P–O(4)–Cu(2′) | 121·3 (2) |
| O(4)–Cu(2′) | 2·019 (3) | Cu(2)–O(4)–Cu(2′) | 98·7 (1) |

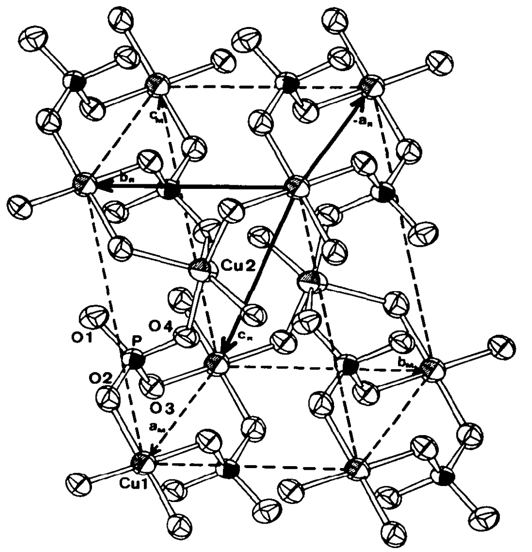

Fig. 1. The unit cell of $Cu_3(PO_4)_2$ with symmetry $P\bar{1}$. The axes of the triacute reduced cell ($-a_R$,$b_R$,$c_R$) are shown by heavy black lines. The morphologically significant unit cell ($a_M$,$b_M$,$c_M$) is shown with dashed lines.

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# (1*SR*,*SRS*)-1-(1-Phenylsulphinylcyclohexyl)ethanol

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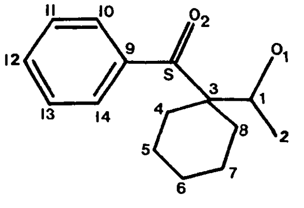
**Abstract.** $C_{14}H_{20}O_2S$, $M_r = 252{\cdot}39$, monoclinic, $P2_1/c$, $a = 13{\cdot}300$ (1), $b = 9{\cdot}760$ (2), $c = 10{\cdot}802$ (3) Å, $\beta = 101{\cdot}51$ (2)°, $V = 1373{\cdot}6$ (5) Å$^3$, $Z = 4$, $D_x = 1{\cdot}220$ g cm$^{-3}$, $\mu = 19{\cdot}35$ cm$^{-1}$ for Cu $K\alpha$ radiation ($\lambda = 1{\cdot}54178$ Å). The structure was refined to $R = 0{\cdot}043$ for 1638 counter reflexions. The relative stereochemistry of the molecule is (1*SR*,*SRS*).

**Introduction.** As part of a continuing study of stereospecific rearrangements (Allen, Kennard, Nassimbeni, Shepherd & Warren, 1974) we have carried out an X-ray analysis of the title compound (I) (Brownbridge, Hodgson, Shepherd & Warren, 1976) to establish the relative stereochemistry at the chiral centres C(1) and S.



(I)

Intensities were collected with Cu $K\alpha$ radiation on a Syntex $P2_1$ diffractometer equipped with a graphite-crystal monochromator. 2358 reflexions were measured up to $2\theta = 120°$; 1994 with $F > 4\sigma(F)$ were classified as observed. Equivalent reflexions were averaged to yield 1638 unique observations. Cell parameters were obtained by least squares from diffractometer measurements for 15 strong high-order reflexions. The structure was solved by a multisolution sign expansion technique (Sheldrick, 1977). The highest 17 peaks from the $E$ map corresponding to the best sign set yielded the positions of the 17 non-hydrogen atoms. Anisotropic refinement of all C, O and S atoms converged to $R = 0{\cdot}082$. All 20 H atoms were located in a subsequent difference map and were refined without constraints.

Table 1. *Fractional atomic coordinates* ($\times 10^4$)

| | $x$ | $y$ | $z$ |
|---|---|---|---|
| S(1) | 1774 (1) | 71 (1) | 900 (1) |
| O(1) | 3811 (2) | −1659 (4) | 1382 (3) |
| O(2) | 2152 (2) | −583 (2) | 2174 (2) |
| C(1) | 3517 (2) | −1039 (4) | 195 (3) |
| C(2) | 4074 (3) | −1780 (6) | −689 (5) |
| C(3) | 2336 (2) | −996 (3) | −247 (2) |
| C(4) | 1842 (2) | −2408 (3) | −194 (3) |
| C(5) | 687 (3) | −2425 (4) | −683 (4) |
| C(6) | 414 (3) | −1848 (4) | −2001 (4) |
| C(7) | 842 (3) | −423 (4) | −2067 (4) |
| C(8) | 2003 (3) | −396 (4) | −1574 (3) |
| C(9) | 2447 (2) | 1663 (3) | 909 (3) |
| C(10) | 3289 (2) | 1948 (4) | 1838 (3) |
| C(11) | 3767 (3) | 3205 (4) | 1853 (4) |
| C(12) | 3397 (4) | 4161 (4) | 927 (4) |
| C(13) | 2544 (4) | 3883 (4) | 17 (4) |
| C(14) | 2064 (3) | 2640 (3) | 8 (3) |

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