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Structure of Copper(II) Diiron(III) Dihydroxide Diarsenate(V)

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Abstract. $CuFe_2(OH)_2(AsO_4)_2$, $M_r = 487{\cdot}08$, orthorhombic, *Pbca*, $a = 7{\cdot}717\,(3)$, $b = 13{\cdot}225\,(5)$, $c = 14{\cdot}549\,(5)$ Å, $V = 1484{\cdot}8$ Å^3, $Z = 8$, $D_x = 4{\cdot}36$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 15{\cdot}2$ mm^{-1}, $F(000) = 1832$, room temperature, $wR = 0{\cdot}028$ for 2176 reflections with $(\sin\theta)/\lambda \le 0{\cdot}70$ Å^{-1}. The Cu^{II} atom and the two Fe^{III} atoms are 'octahedrally' [6] coordinated by O atoms; the CuO_6 polyhedron shows the typical Jahn–Teller distortion with four 'short' Cu—O bonds (average 2·003 Å) and two 'long' Cu—O bonds (~2·35 Å); the Fe—O bond lengths vary from 1·916 (3) to 2·180 (3) Å; average values are 2·018 Å. The FeO_6 octahedra form chains in [100] *via* common O_h atom corners. The CuO_6 polyhedron shares two faces with FeO_6 polyhedra in different chains. The connection results in rugged layers parallel to (010) with formula ${}^2_\infty[CuFe_2(O_h)_2O_8]^{6-}$. The layers are connected by arsenate tetrahedra and hydrogen bonds to form a framework.

Introduction. As part of a continuing study of the crystal chemistry of copper(II) arsenates(V) (Effenberger, 1987, 1988*a*,*b*; Effenberger & Pertlik, 1987; Pertlik, 1987) the crystal structure of $CuFe_2(OH)_2(AsO_4)_2$ was determined. Crystals suitable for single-crystal X-ray work were grown under hydrothermal conditions. Recently the new mineral hentschelite, $CuFe_2(OH)_2(PO_4)_2$ was described by Sieber, Tillmanns & Medenbach (1987); its crystal structure was determined by Sieber, Tillmanns & Hofmeister (1987). The crystal structures of the title compound and of hentschelite show some crystal chemical relations.

Experimental. For synthesis of $CuFe_2(OH)_2(AsO_4)_2$ 2 g of an equimolar mixture of CuO, Fe_2O_3 and As_2O_3 were placed in a vessel lined with 'Teflon'; H_2O was added to 80 vol.%. Black crystals were produced after 3 d at 500 (10) K. In very thin sections they are dark brownish green and fairly transparent. Weissenberg photographs revealed orthorhombic symmetry: from extinction rules space group *Pbca* was derived; well developed crystallographic forms are {102} and {011}, and the crystals are elongated parallel to [010] (length ≤ 1 mm, diameter ≤ 0·3 mm).

Synthetic crystal, 0·07 × 0·07 × 0·22 mm; four-circle diffractometer AED2 (Stoe & Cie, Darmstadt, Federal Republic of Germany), graphite-monochromatized Mo $K\alpha$ radiation; lattice parameters from 74 reflections with $2\theta \le 53°$; $2\theta/\omega$ scan mode, minimum of 55 steps per reflection increased for α_1–α_2 splitting, step width 0·03°, step time 0·5 to 1·5 s per step, nine steps each side for background correction; drift correction of max. 6·6% based on three standard reflections; 4833 reflections with $2\theta \le 60°$ (h: 0→10, k: 0→18, l: −20→20), 2176 reflections in unique data set ($R_{\rm int} = 0{\cdot}055$); four ψ scans for empirical absorption correction (transmission factors: 0·535 to 0·640), corrections for Lorentz and polarization effects. Complex neutral-atom scattering functions (*International Tables for X-ray Crystallography*, 1974). All calculations were performed with the program system *STRUCSY* (Stoe & Cie, 1984) on an Eclipse S140 computer (Data General). Some of the atomic coordinates of the As, Cu and Fe atoms were located by direct methods, the O atoms and the H atoms by subsequent difference Fourier summations. Several cycles of least-squares refinements on F with anisotropic temperature parameters (for the hydrogen atoms $U_{\rm iso}$ was fixed to 0·01 Å^2); $R = 0{\cdot}070$, $wR = 0{\cdot}028$; for refinement with 1554 reflections having $F_o > 3\sigma(F_o)$ $R = 0{\cdot}039$, $wR = 0{\cdot}027$; $w = [\sigma(F_o)]^{-2}$ (143 variables), goodness of fit 1·6; max. $\Delta/\sigma < 10^{-3}$; max. and min. heights in final difference Fourier map 1·4 and −1·2 e Å^{-3}; extinction correction was negligible. The final atomic coordinates and equivalent isotropic temperature parameters are given in Table 1.* Table 2 gives some important interatomic distances and bond angles.

Discussion. The Cu^{II} atom is [4+2] coordinated by four near O atoms forming an approximate square (average Cu—O bond distance 2·003 Å); the two

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* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51183 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic fractional coordinates with e.s.d.'s in parentheses and equivalent isotropic temperature parameters* (Å^2)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Cu	0·37149 (8)	0·37779 (5)	0·12496 (4)	0·0123
Fe(1)	−0·02534 (9)	0·01151 (6)	0·26086 (5)	0·0090
Fe(2)	0·22136 (11)	0·23827 (6)	−0·00584 (4)	0·0096
As(1)	0·24321 (6)	0·00337 (4)	0·44167 (3)	0·0087
As(2)	−0·01728 (6)	0·25344 (4)	0·19295 (3)	0·0088
O(11)	0·0547 (5)	−0·0001 (3)	0·3857 (2)	0·016
O(12)	0·4153 (5)	0·0065 (3)	0·3708 (2)	0·017
O(13)	0·2678 (5)	−0·0951 (3)	0·5140 (2)	0·013
O(14)	0·2467 (4)	0·1073 (3)	0·5090 (2)	0·011
O(21)	−0·1964 (5)	0·2573 (3)	0·1301 (2)	0·016
O(22)	0·1624 (4)	0·2508 (3)	0·1284 (2)	0·012
O(23)	−0·0210 (5)	0·1580 (3)	0·2683 (3)	0·014
O(24)	−0·0058 (4)	0·3583 (3)	0·2599 (2)	0·014
O$_h$(1)	0·2263 (5)	0·0010 (2)	0·1934 (2)	0·011
O$_h$(2)	−0·0245 (4)	0·2444 (3)	−0·0557 (3)	0·013
H(1)	0·228 (8)	0·031 (5)	0·168 (4)	0·01†
H(2)	−0·018 (8)	0·289 (4)	−0·096 (4)	0·01†

† Fixed during refinement.

Table 2. *Interatomic distances* (Å) *and bond angles* (°)

Cu$^{\rm i}$—O(24$^{\rm v}$)	1·941 (3)	O$_h$(1$^{\rm viii}$)—O(12$^{\rm iv}$)	2·577 (5) (*a*)
Cu$^{\rm i}$—O(14$^{\rm ii}$)	1·953 (3)	O$_h$(1$^{\rm viii}$)—O(24$^{\rm v}$)	2·630 (5) (*a*)
Cu$^{\rm i}$—O$_h$(1$^{\rm viii}$)	2·053 (3)	O(12$^{\rm iv}$)—O(24$^{\rm v}$)	2·633 (5) (*a*)
Cu$^{\rm i}$—O$_h$(2$^{\rm ix}$)	2·066 (3)	O$_h$(2$^{\rm ix}$)—O(14$^{\rm ii}$)	2·621 (5) (*b*)
Cu$^{\rm i}$—O(12$^{\rm iv}$)	2·368 (3)	O$_h$(2$^{\rm ix}$)—O(22$^{\rm i}$)	2·638 (5) (*b*)
Cu$^{\rm i}$—O(22$^{\rm i}$)	2·329 (3)	O(14$^{\rm ii}$)—O(22$^{\rm i}$)	2·638 (5) (*b*)
Fe(1$^{\rm i}$)—O(11$^{\rm i}$)	1·924 (3)	Fe(2$^{\rm i}$)—O(21$^{\rm ix}$)	1·916 (3)
Fe(1$^{\rm i}$)—O(23$^{\rm i}$)	1·940 (3)	Fe(2$^{\rm i}$)—O(13$^{\rm vii}$)	1·917 (3)
Fe(1$^{\rm i}$)—O(12$^{\rm vi}$)	1·971 (3)	Fe(2$^{\rm i}$)—O(22$^{\rm i}$)	2·012 (3)
Fe(1$^{\rm i}$)—O$_h$(1$^{\rm vi}$)	2·033 (3)	Fe(2$^{\rm i}$)—O$_h$(2$^{\rm v}$)	2·033 (3)
Fe(1$^{\rm i}$)—O(24$^{\rm iii}$)	2·062 (4)	Fe(2$^{\rm i}$)—O(14$^{\rm ii}$)	2·063 (3)
Fe(1$^{\rm i}$)—O$_h$(1$^{\rm i}$)	2·180 (3)	Fe(2$^{\rm i}$)—O$_h$(2$^{\rm ix}$)	2·168 (3)
Mean	2·018	Mean	2·018
As(1$^{\rm i}$)—O(11$^{\rm i}$)	1·668 (3)	As(2$^{\rm i}$)—O(21$^{\rm i}$)	1·659 (3)
As(1$^{\rm i}$)—O(12$^{\rm i}$)	1·682 (3)	As(2$^{\rm i}$)—O(22$^{\rm i}$)	1·675 (3)
As(1$^{\rm i}$)—O(13$^{\rm i}$)	1·685 (3)	As(2$^{\rm i}$)—O(23$^{\rm i}$)	1·672 (3)
As(1$^{\rm i}$)—O(14$^{\rm i}$)	1·688 (3)	As(2$^{\rm i}$)—O(24$^{\rm i}$)	1·697 (3)
Mean	1·681	Mean	1·676
O$_h$(1$^{\rm i}$)—H(1$^{\rm i}$)	0·55 (6)	O$_h$(2$^{\rm i}$)—H(2$^{\rm i}$)	0·83 (6)
O$_h$(1$^{\rm i}$)···O(13$^{\rm vii}$)	2·893 (5)	O$_h$(2$^{\rm i}$)···O(23$^{\rm ii}$)	2·867 (5)
H(1$^{\rm i}$)···O(13$^{\rm vii}$)	2·39 (6)	H(2$^{\rm i}$)···O(23$^{\rm ii}$)	2·10 (6)
O$_h$(1$^{\rm i}$)—H(1$^{\rm i}$)···O(13$^{\rm vii}$)	154 (8)	O$_h$(2$^{\rm i}$)—H(2$^{\rm i}$)···O(23$^{\rm ii}$)	154 (7)

O—O edges defining common faces between the coordination polyhedra (*a*) CuO$_6$ and Fe(1)O$_6$ and (*b*) CuO$_6$ and Fe(2)O$_6$.

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

Cu—O$_h$ bond lengths (~2·06 Å) are definitely longer than the two bonds to O atoms belonging to the arsenate tetrahedra (Cu—O~1·95 Å). The two distant O atoms have Cu—O~2·35 Å. Because of the Jahn–Teller effect the 'octahedral' coordination figure is distorted to an elongated tetragonal bipyramid. The two Fe$^{\rm III}$ atoms are octahedrally coordinated by O atoms, each with an average Fe—O bond distance of 2·018 Å; the individual Fe—O bond lengths range from 1·916 (3) to 2·180 (3) Å. As usual the arsenate groups form tetrahedra with As—O bond lengths from 1·659 (3) to 1·697 (3) Å (average 1·681 and 1·676 Å), O—O edges from 2·655 (5) to 2·793 (5) Å, and O—As—O angles from 104·0 (2) to 113·0 (2)°. The bond length distortion $\Delta = \frac{1}{4}\sum_{i=1}^{4}[(R_i-R)/R]^2$ is $2{\cdot}08\times10^{-5}$ and $6{\cdot}59\times10^{-5}$, the bond angle variance $\sigma^2 = \frac{1}{5}\sum_{i=1}^{6}(\theta_i-109{\cdot}47)^2$ is 8·05 and 10·68 for the As(1)O$_4$ and As(2)O$_4$ tetrahedra (Robinson, Gibbs & Ribbe, 1971; Fleet, 1976).

The FeO$_6$ octahedra are linked by O$_h$ atom corners to form Fe(O$_h$)O$_4$ chains in [100], Fe(1)—O$_h$(1)—Fe(1) = 133·5 (2)°, Fe(2)—O$_h$(2)—Fe(2) = 134·5 (2)°. An interesting detail in the crystal structure of CuFe$_2$(OH)$_2$(AsO$_4$)$_2$ is the connection of the iron and copper coordination polyhedra: CuO$_6$ shares opposite faces with one Fe(1)O$_6$ and one Fe(2)O$_6$ octahedron in

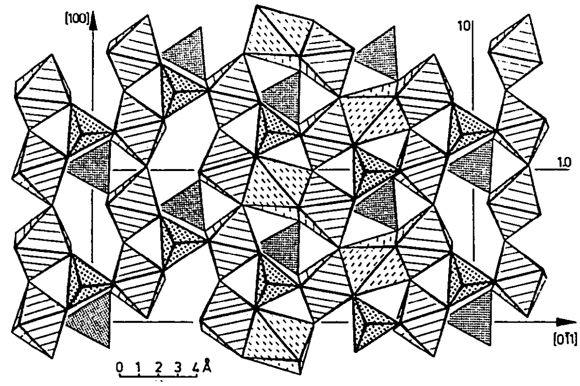

Fig. 1. Detail of the crystal structure of CuFe$_2$(OH)$_2$(AsO$_4$)$_2$. The coordination polyhedra of CuO$_6$ are stippled, FeO$_6$ octahedra are hatched, and AsO$_4$ tetrahedra are dotted.

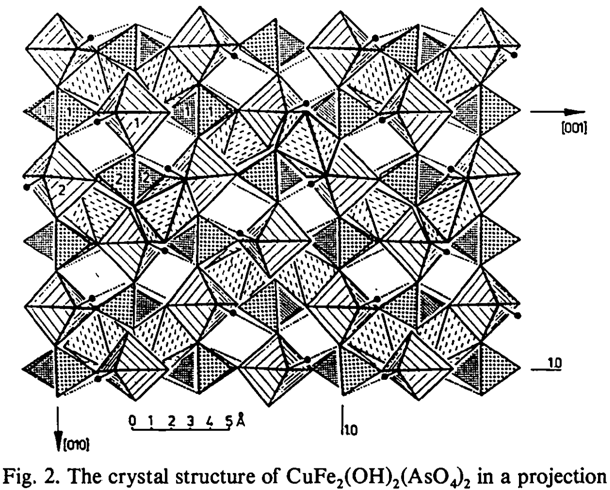

Fig. 2. The crystal structure of CuFe$_2$(OH)$_2$(AsO$_4$)$_2$ in a projection onto (100) showing the connection of the rugged CuFe$_2$(O$_h$)$_2$O$_8$ layers (CuO$_6$ polyhedra are stippled, FeO$_6$ octahedra are hatched) with the AsO$_4$ tetrahedra (dotted) and hydrogen bonds. The indexes for a few iron and arsenic atoms are indicated.

different $Fe(O_h)O_4$ chains building formal $CuFe_2(O_h)_4O_8$ groups (see Fig. 1). The connection causes a shortening of the O—O edges defining the common faces: the shared O—O edges vary from 2·577 (5) to 2·638 (5) Å, the unshared ones vary from 3·010 (5) to 3·587 (5) Å in the CuO_6 polyhedron and from 2·702 (5) to 3·095 (5) Å in the $Fe(1)O_6$ and $Fe(2)O_6$ octahedra. The angles between two O atoms defining the common faces [O—Cu—O from 70·9 (1) to 82·3 (2)°, O—Fe—O from 76·5 (1) to 81·5 (2)°] are smaller than the other angles [O—Cu—O from 97·3 (2) to 107·9 (1)°, O—Fe—O from 86·9 (2) to 99·1 (2)°]. Considering the connection of the [6]-coordinated cations in $CuFe_2(OH)_2(AsO_4)_2$ the crystal structure consists of rugged layers parallel to (010). They are connected by the hydrogen bonds and arsenate tetrahedra (see Fig. 2).

The title compound contains pairs of atoms which have topologically the same environment: Fe(1)—Fe(2), As(1)—As(2), O(11)—O(21), O(12)—O(22), O(13)—O(23), O(14)—O(24), $O_h(1)$—$O_h(2)$, and H(1)—H(2). Neglecting the Cu and H atoms a theoretical cell with $a' = a$, $b' = b/2$, and $c' = c/2$, and $Z' = Z/4$ results.

The mineral hentschelite, $CuFe_2(OH)_2(PO_4)_2$, crystallizes in space group $P2_1/n$ ($a = 6·98$, $b = 7·79$, $c = 7·27$ Å, $\beta = 117·68°$; Sieber, Tillmanns & Hofmeister, 1987; Sieber, Tillmanns & Medenbach, 1987). Hentschelite is isostructural with the lazulite group minerals (Lindberg & Christ, 1959). Both the polymorphs show some structural relationships: they contain formal groups $CuFe_2(O_h)_4O_8$ formed by the face-shared polyhedra FeO_6—CuO_6—FeO_6; the $Fe(O_h)_2O_4$ octahedra are linked through corner-shared O_h atoms to form rows, the coordination polyhedra $Cu(O_h)_2O_4$ and $Fe(O_h)_2O_4$ form complicated sheets which are linked by XO_4 tetrahedra ($X = $ P and As, respectively) and by hydrogen bonds to form a three-dimensional framework. The distinction between the crystal structures of hentschelite and of the title compound depends on the different periodicity found for the rugged sheets. The different wave pattern gives rise to the different symmetries.

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Structure of Lead(II) Arsenate(III)

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Abstract. $PbAs_2O_4$, $M_r = 421·04$, monoclinic, $P2_1/c$, $a = 7·037$ (3), $b = 11·801$ (6), $c = 6·137$ (3) Å, $\beta = 112·99$ (3)°, $V = 469·2$ (2) Å^3, $Z = 4$, $D_x = 5·96$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0·71073$ Å, $\mu = 48·2$ mm^{-1}, $F(000) = 720$, room temperature, $R(F) = 0·047$ for 1654 independent reflections with $F_o > 4\sigma(F_o)$ and 65 variables. The crystal structure of $PbAs_2O_4$ consists of AsO_3 pyramids which are corner connected to form As_4O_8 rings with symmetry $\bar{1}$, bonding As—O distances from 1·790 (10) to 1·833 (9) Å, and branched As—O bond distances 1·726 (8) and 1·735 (8) Å. The As_4O_8 rings are connected by the Pb atoms to form a framework. The Pb atom has four ligands: 2·250 (8) ≤ Pb—O ≤ 2·500 (8) Å; further Pb—O distances

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