

Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: HU1145). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Polytypism of CuFe₂(OH)₂(AsO₄)₂: the Triclinic Modification

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Abstract

The triclinic modification of dimorphic CuFe₂(OH)₂(AsO₄)₂ is presented. The O atoms are cubic close packed; between succeeding layers only alternate octahedral or tetrahedral positions are occupied. Within the 'octahedral sheets', Cu^[4+2](O_h)₂O₄ and Fe^[6](O_h)₂O₄ (O_h = hydroxyl O atom) polyhedra are edge-connected

to form bands; 2/5 of the positions are vacant. These □O₆ octahedra each share one face with an AsO₄ anion of the 'tetrahedral sheet'; bifurcated hydrogen bonds link neighbouring octahedral sheets.

Comment

A number of structure types for compounds with the general formula $M^{2+}M_2^{3+}(\text{OH})_2(\text{XO}_4)_2$ ($X = \text{P}, \text{As}$) have been described. The most prominent is the monoclinic lazulite-type known from several minerals: lazulite, MgAl₂(OH)₂(PO₄)₂ (Giuseppetti & Tadini, 1983), scorzalite, (Fe,Mg)Al₂(OH)₂(PO₄)₂ (Lindberg & Christ, 1959), barbosalite, Fe₃(OH)₂(PO₄)₂ (Lindberg & Christ, 1959), and hentschelite, CuFe₂(OH)₂(PO₄)₂ (Sieber, Tillmanns & Hofmeister, 1987). Even the substitution of M^{3+} by M^{2+} combined with the incorporation of a protonated XO₃OH group has been described: Co₃(OH)₂(PO₃OH)₂ (Effenberger, 1992). Lazulite-type arsenates are unknown.

With cations of larger atomic radii and, therefore, higher coordination numbers, the structure type changes, e.g. jagowerite, BaAl₂(OH)₂(PO₄)₂ (Meagher, Gibbons & Trotter, 1974), and carminite, PbFe₂(OH)₂(AsO₄)₂ (Finney, 1963). Moreover, Fe₃(OH)₂(PO₄)₂ forms a tetragonal polytype (lipscombit; Vencato, Mattievich & Mascarenhas, 1989).

The orthorhombic modification of CuFe₂(OH)₂(AsO₄)₂ (Effenberger, 1988) is closely related to the lazulite structure type: one $M^{2+}(\text{O}_h)_2\text{O}_4$ and two $M^{3+}(\text{O}_h)_2\text{O}_4$ octahedra share faces to form $M^{2+}M_2^{3+}(\text{O}_h)_4\text{O}_8$ trimers. The $M^{3+}(\text{O}_h)_2\text{O}_4$ octahedra are linked via O_h atoms into chains. As a result, corrugated sheets are formed with the undulations in the two phases being different. The layers are interconnected by XO₄ tetrahedra and by hydrogen bonds.

In triclinic CuFe₂(OH)₂(AsO₄)₂ (Fig. 1), the modes of coordination are as usual. The Cu^{II} atom has site symmetry $\bar{1}$ and is [4 + 2] coordinated to form an elongated octahedron, showing characteristic Jahn–Teller distortions due to the d^9 electronic configuration (Norrestam, 1994). The two Cu—O_h bonds are the shortest bonds within this polyhedron; the average bond length within the square formed by the four nearest neighbours is 1.957 Å. The additional bonds are almost 2.50 Å in length, indicating only weak interactions. The Fe(O_h)₂O₄ octahedron is less distorted. The longest bonds are to the O_h atoms. Contrary to the orthorhombic polytype the O_h atoms are in a *cis* arrangement. The average Fe—L bond length of 2.017 Å is in accordance with expectations for the trivalent oxidation state (*L* is an unspecified ligand belonging either to the arsenate group or to the hydroxyl group). The arsenate tetrahedron has an average As—O bond length of 1.687 Å. As a result of face-to-face connection, orthorhombic CuFe₂(OH)₂(AsO₄)₂ shows stronger distortion of the coordination polyhedra.

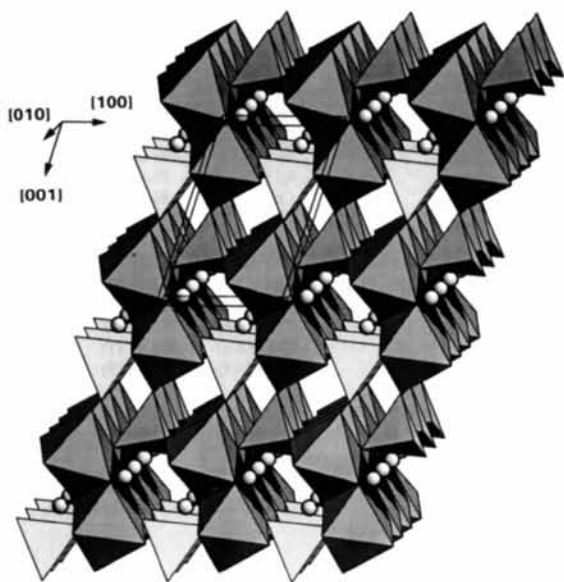


Fig. 1. Projection slightly inclined to [010]. $\text{Fe}^{6+}L_6$ and $\text{Cu}^{4+2}L_6$ octahedra are light and dark shaded; spheres represent H atoms.

The atoms O(1) and O(3) are coordinated to a Cu, an Fe and an As atom; O(2) and O(4) are coordinated to one Fe and one As atom. In addition, O(1) and O(2) are the acceptors of a bifurcated hydrogen bond from the hydroxyl group. The O_h atom is pyramidally surrounded by two Fe atoms and by one Cu atom; the H atom is out of the plane defined by the three cations. The H atom was located experimentally; uncertainties in its position are reflected in the observed $\text{O}_h\text{—H}$ bond length, which is obviously too short. Bond valences ν_{ij} (according to Brese & O'Keeffe, 1991) agree with these results: excluding the contribution of the H atom, O_h has $\sum \nu_{ij} = 1.28$ valence units [v.u.], the acceptors O(1) and O(2) have $\sum \nu_{ij} = 1.89$ and 1.91 v.u., whereas the atoms O(3) and O(4) have $\sum \nu_{ij} = 2.08$ and 1.95 v.u. The hydrogen bond with two contacts of almost similar length compares well with that of the lazulite structure type. In contrast, in orthorhombic $\text{CuFe}_2(\text{OH})_2(\text{AsO}_4)_2$ common $\text{O}_h\text{—H}\cdots\text{O}$ bonds have been described.

The L atoms in triclinic $\text{CuFe}_2(\text{OH})_2(\text{AsO}_4)_2$ are slightly distorted cubic close packed. The most prominent of the four different c.c.p. layer sequences is parallel to $(10\bar{1})$. Between these layers, only alternate octahedral or tetrahedral sites are occupied (the environment of the Cu atom is considered to be octahedral). $\text{Cu}(\text{O}_h)_2\text{O}_4$ and $\text{Fe}(\text{O}_h)_2\text{O}_4$ octahedra are edge-connected to form $\text{CuFe}_2(\text{O}_h)_2\text{O}_8$ bands running parallel to [010]. L atoms belonging to three cations are O_h atoms. Including the vacant octahedral positions \square , brucite-like $\text{CuFe}_2\square_2(\text{O}_h)_2\text{O}_8$ sheets are formed. Alternating top and bottom faces of $\square\text{O}_6$ octahedra are shared with arsenate tetrahedra [atoms O(1), O(2), O(4)]; the

AsO_4 tetrahedra point out of the plane of octahedral sheet. The remaining O atom O(3) represents the fourth apex of an arsenate tetrahedron (Fig. 2.) The hydrogen bond crosses the tetrahedral sheet. The morphology is in accordance with these connections: crystals are elongated parallel to [010]; the crystallographic forms $\{001\}$ (largest faces) and $\{10\bar{1}\}$ were observed.

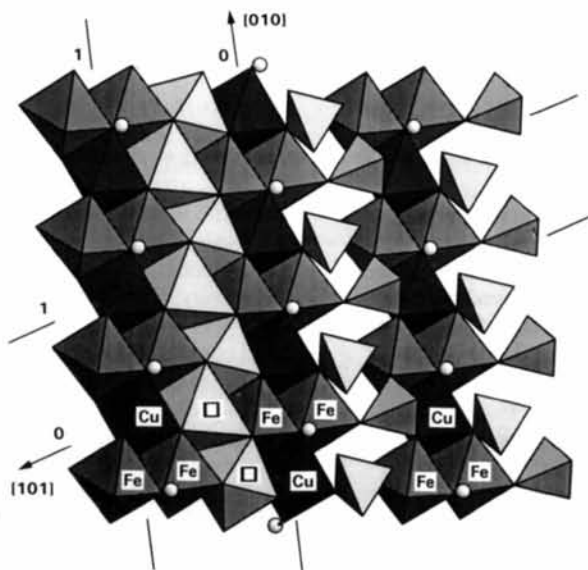


Fig. 2. Projection approximately on $(10\bar{1})$. Left: the brucite-like $\text{CuFe}_2\square_2(\text{O}_h)_2\text{O}_8$ layer formed by $\text{Cu}(\text{O}_h)_2\text{O}_4$ (dark), $\text{Fe}(\text{O}_h)_2\text{O}_4$ (medium) and $\square\text{O}_6$ (light) octahedra; right: the AsO_4 tetrahedra above the $\text{CuFe}_2(\text{O}_h)_2\text{O}_8$ band.

Similar M_3L_{10} chains have been described, e.g. in lindgreenite, $\text{Cu}_3(\text{OH})_2(\text{MoO}_4)_2$ (Hawthorne & Eby, 1985), where neighbouring chains are inclined towards one another. In kotoite, $\text{Mg}_3(\text{BO}_3)_2$, and its isotypic Mn, Co and Ni analogues (Bondareva, Simonov & Belov, 1978; Effenberger & Pertlik, 1984) the M_3L_{10} chains are corner connected to one another.

Experimental

Hydrothermal synthesis of triclinic $\text{CuFe}_2(\text{OH})_2(\text{AsO}_4)_2$ was performed successfully during investigations of the system $\text{Pb}(\text{CH}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}\text{—Fe}_2\text{O}_3\text{—Cu}(\text{OH})_2\text{—As}_2\text{O}_5$. 2 g of the appropriate mixture was ground and heated with 2 ml of H_2O to 503 K during 5 d in Teflon-lined stainless steel autoclaves of approximately 7 ml capacity. Afterwards, the vessels were cooled for 12 h to room temperature.

Crystal data

$\text{CuFe}_2(\text{OH})_2(\text{AsO}_4)_2$
 $M_r = 487.08$

Mo $K\alpha$ radiation
 $\lambda = 0.71069 \text{ \AA}$

Triclinic	Cell parameters from 82 reflections
$P\bar{1}$	$\theta = 18.0\text{--}25.7^\circ$
$a = 5.094(2)\text{ \AA}$	$\mu = 16.3\text{ mm}^{-1}$
$b = 5.273(2)\text{ \AA}$	Room temperature
$c = 7.572(3)\text{ \AA}$	Elongated $\ [010]$; forms: $\{001\}$ (large), $\{\bar{1}01\}$
$\alpha = 102.52(2)^\circ$	$0.143 \times 0.076 \times 0.042\text{ mm}$
$\beta = 104.45(2)^\circ$	Light green
$\gamma = 102.07(2)^\circ$	
$V = 184.7\text{ \AA}^3$	
$Z = 1$	
$D_x = 4.48\text{ Mg m}^{-3}$	
Data collection	
Stoe AED-2 diffractometer	$R_{\text{int}} = 0.018$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 30^\circ$
Absorption correction: empirical (ψ scan)	$h = -7 \rightarrow 7$
$T_{\text{min}} = 0.082$, $T_{\text{max}} = 0.182$	$k = -7 \rightarrow 7$
2172 measured reflections	$l = -10 \rightarrow 10$
1072 independent reflections	3 standard reflections
953 observed reflections	frequency: 120 min
$[F > 2.0\sigma(F)]$	intensity decay: 1.02%

Refinement

Refinement on F	Extinction correction: isotropic secondary
$R = 0.020$	Extinction coefficient: 0.00132
$wR = 0.019$	Atomic scattering factors from <i>International Tables for Crystallography</i> (1992, Vol. C)
953 reflections	
76 parameters	
H atoms refined isotropically	
$w = 0.716/\sigma^2(F)$	
$(\Delta/\sigma)_{\text{max}} < 0.001$	
$\Delta\rho_{\text{max}} = 0.59\text{ e \AA}^{-3}$	
$\Delta\rho_{\text{min}} = -0.87\text{ e \AA}^{-3}$	

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

B_{iso} for H; $B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i a_j$ (Fischer & Tillmanns, 1988) for non-H atoms.

	x	y	z	B_{eq}
Cu	0	0	0	0.84 (2)
Fe	0.22336 (9)	0.59357 (9)	0.22399 (6)	0.66 (2)
As	0.68251 (6)	0.20797 (6)	0.31085 (5)	0.64 (1)
O(1)	0.4418 (5)	-0.0841 (4)	0.1729 (3)	0.99 (7)
O(2)	0.5575 (5)	0.4741 (4)	0.2911 (4)	1.12 (7)
O(3)	0.9663 (4)	0.2409 (4)	0.2274 (3)	0.81 (7)
O(4)	0.7951 (5)	0.2072 (5)	0.5378 (3)	1.14 (7)
O _h	0.8735 (5)	0.6647 (5)	0.0595 (4)	0.86 (7)
H	0.778 (8)	0.660 (9)	0.091 (6)	0.8 (8)

Table 2. Interatomic bonds, intrapolyhedral ligand–central atom–ligand angles and ligand–ligand distances (\AA , $^\circ$)

Common edges are between: (*) a Cu^[4+2](O_h)₂O₄ and an Fe^[6](O_h)₂O₄ polyhedron, as well as (†) two Fe^[6](O_h)₂O₄ polyhedra.

Cu—O _h ^{i,ii}	1.939 (2)	O _h ⁱ ,O(3 ^{iv})	83.70 (8)	2.611 (3)*
Cu—O(3 ^{iii,iv})	1.974 (2)	O _h ⁱ ,O(1)	75.60 (6)	2.745 (2)*
Cu—O(1 ^v)	2.485 (2)	O(3 ^{iv}),O(1)	85.15 (7)	3.040 (3)
Fe—O(4 ^{vi})	1.916 (2)	O(4 ^{vi}),O(2)	104.37 (9)	3.034 (2)
Fe—O(2)	1.925 (1)	O(4 ^{vi}),O(1 ^{vi})	94.72 (8)	2.878 (3)

Fe—O(1 ^{vi})	1.996 (2)	O(4 ^{vi}),O(3 ⁱⁱⁱ)	93.24 (8)	2.882 (3)
Fe—O(3 ⁱⁱⁱ)	2.048 (1)	O(4 ^{vi}),O _h ⁱⁱⁱ	95.47 (8)	2.944 (3)
Fe—O _h ⁱⁱⁱ	2.060 (2)	O(2),O(1 ^{vi})	90.71 (6)	2.791 (2)
Fe—O _h ⁱⁱ	2.152 (2)	O(2),O(3 ⁱⁱⁱ)	92.78 (6)	2.878 (2)
		O(2),O _h ⁱⁱ	87.52 (8)	2.825 (3)
		O(1 ^{vi}),O _h ⁱⁱⁱ	85.17 (7)	2.745 (2)*
		O(1 ^{vi}),O _h ⁱⁱ	94.21 (8)	3.041 (3)
		O(3 ⁱⁱⁱ),O _h ⁱⁱ	76.85 (8)	2.611 (3)
		O(3 ⁱⁱⁱ),O _h ⁱⁱⁱ	88.45 (7)	2.865 (2)*
		O _h ⁱⁱⁱ ,O _h ⁱⁱ	73.32 (7)	2.516 (2)†
As—O(4)	1.672 (2)	O(4),O(2)	111.45 (10)	2.768 (3)
As—O(2)	1.678 (2)	O(4),O(1)	112.11 (9)	2.785 (3)
As—O(1)	1.685 (2)	O(4),O(3)	107.78 (8)	2.731 (3)
As—O(3)	1.708 (1)	O(2),O(1)	111.01 (8)	2.772 (2)
		O(2),O(3)	106.87 (7)	2.720 (2)
		O(1),O(3)	107.34 (9)	2.734 (2)
H—O _h	0.59 (3)	O _h ,O(2)	145 (4)	2.858 (3)
H...O(2)	2.35 (3)	O _h ,O(1 ^{vi})	143 (4)	2.999 (2)
H...O(1 ^{vi})	2.50 (3)	O(2),O(1 ^{vi})	70.1 (8)	2.791 (2)

Symmetry codes: (i) $x - 1, y - 1, z$; (ii) $1 - x, 1 - y, -z$; (iii) $x - 1, y, z$; (iv) $1 - x, -y, -z$; (v) $-x, -y, -z$; (vi) $1 - x, 1 - y, 1 - z$; (vii) $x, 1 + y, z$.

The structure was solved by Patterson and Fourier methods. H atoms were found in a difference Fourier summation and refined isotropically. All refinements were by full-matrix least squares.

Programs used: *DIF4* (Stoe & Cie, 1992) for data collection, cell refinement and data reduction; *SHELX76* (Sheldrick, 1976) for structure refinement; *ATOMS* (Dowty, 1991) for molecular graphics.

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Lists of structure factors and anisotropic displacement parameters have been deposited with the IUCr (Reference: JZ1007). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Reconciling the Crystal Structure of $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ with its ESR Properties

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Abstract

Hexaammineruthenium(III) trichloride forms a $Z = 12$ monoclinic crystal, which is related to a simple cubic f.c.c. structure by, dominantly, a rotation of a third of the hexaammineruthenium(III) fragments. The cell contains four crystallographically inequivalent $\text{Ru}(\text{NH}_3)_6$ fragments, but two are almost identical in conformation and orientation in the crystal. In the ESR spectrum only three resolvable crystallographically different ions are thus predicted, not four. This is what is observed.

Comment

We are engaged in a study of the relation between structure and ESR properties in a series of hexaammineruthenium(III) salts containing a single crystallographically unique Ru site (Blake *et al.*, 1993; Engelhardt, Reynolds & Sobolev, 1994; Figgis, Kucharski, Reynolds & Sobolev, 1993; Reynolds *et al.*, 1992).

A detailed crystal structure is required to eliminate a possible anomaly in the case of $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$. Four independent Ru sites are inferred from the observed unit cell of $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ (Trehoux, Thomas, Nowogrocki & Tridot, 1971), and four sites are inferred by NMR and X-ray diffraction in the possibly isomorphous Co^{III} salt (Kruger & Reynhardt, 1978; Reynhardt, 1977). However, Griffiths, Owen & Ward (1953) observed only

three crystallographically distinct Ru sites by use of single-crystal ESR.

Stable crystals were grown by recrystallization from a solution of hexaammineruthenium(III) trichloride in dilute hydrochloric acid. However, the first growth of crystals from approximately neutral solution proved to be unstable. Unless contained, for example, in a Lindemann tube, the crystals decomposed to a white powder, possibly by reaction with atmospheric moisture. We determined the crystal structure of both forms, which proved to be identical within experimental error. We report only the results from the stable form.

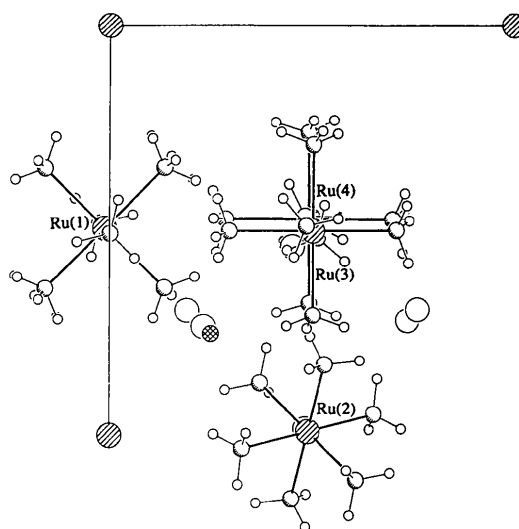


Fig. 1. The four crystallographically independent $\text{Ru}(\text{NH}_3)_6$ fragments and unique Cl and O1w (void site), projected down the underlying cube axis $(-1/2, 0, 1/2)$. Underlying cube axis $(-1/2, 1/3, -1/2)$ horizontal.

We find four independent fully occupied Ru sites: $1/6$ of the total ruthenium on Ru(1), $1/6$ on Ru(2), and $1/3$ each on Ru(3) and Ru(4). The key to obtaining an apparently three-resonance ESR spectrum is to note that in the observed crystal structures the $\text{Ru}(3)(\text{NH}_3)_6$ and $\text{Ru}(4)(\text{NH}_3)_6$ fragments are almost superimposable with no rotation (Fig. 2). The r.m.s. deviations in N-atom positions between the two ions are 0.03 \AA , and for H-atom positions 0.19 \AA . This close coincidence is liable to render the ESR signals from these two ions unresolvable. Thus, although there are four independent Ru sites in the cell, we will only see three ESR signals, just as is observed.

There is an underlying cubic structure in this crystal, and in the isomorphous Co^{III} material, which is closely related to the $Fm\bar{3}m$ structure actually observed in a number of $M^{\text{III}}(\text{NH}_3)_6X_3$ crystals, e.g. $\text{Co}(\text{NH}_3)_6\text{I}_3$ (Wyckoff, 1981). There is an f.c.c. cubic Ru lattice of edge $ca 10.3 \text{ \AA}$. Approximately f.c.c. unit-cell axes are $[-1/2, 0, 1/2]$, $[1/2, 1/3, 1/2]$, $[-1/2, 1/3, -1/2]$ vectors of the monoclinic cell. The Ru—N vectors