In addition it must be noticed that one of the water molecules [O(*W*1)] is not involved in cation coordination.

The drawings have been made using the *STRUPLO* program (Fischer, 1985).

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Room-Temperature Structure of Diaquaoctafluorocopper(II)diiron(III)

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Abstract. $CuFe_2F_8(H_2O)_2$, $M_r = 363{\cdot}25$, monoclinic, $C2/c$, $a = 7{\cdot}541\,(3)$, $b = 7{\cdot}501\,(3)$, $c = 13{\cdot}027\,(7)$ Å, $\beta = 90{\cdot}52\,(4)°$, $V = 736{\cdot}8\,(15)$ Å^3, $Z = 4$, $D_x = 3{\cdot}28$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 6{\cdot}88$ mm^{-1}, $F(000) = 692$, $R = 0{\cdot}036$ for 2321 unique observed reflections, hydrothermal growth. The room-temperature structure of $CuFe_2F_8(H_2O)_2$ derives from that of $Fe_3F_8(H_2O)_2$. It is described in terms of infinite $[FeF_{4/2}F_2]_n$ layers of corner-sharing octahedra connected by copper polyhedra or in terms of shifted $[CuF_{4/2}(H_2O)_2, 2FeF_{6/2}]$ Kagomé layers. Copper octahedra are so strongly distorted {two short Cu—O distances [1·935 (2) Å], two short Cu—F distances [1·909 (1) Å] and two long Cu—F distances [2·451 (2) Å]} that the coordination of copper is better described by a $CuF_2(H_2O)_2$ square plane, as shown by a bond-valence analysis.

Introduction. Several $M^{II}Fe_2F_8(H_2O)_2$ phases with M = Fe, Mn were recently grown by hydrothermal synthesis (Herdtweck, 1983; Leblanc, Ferey, Calage & De Pape, 1984). Owing to the presence in the structure of triangles of corner-sharing octahedra, frustration of antiferromagnetic interactions occurs and peculiar magnetic properties can be observed (Guillot, Marchand, Leblanc & Ferey, 1987), for example, 'idle spin' behaviour of Fe^{2+} was evidenced in $Fe_3F_8(H_2O)_2$. We report here the structure of $CuFe_2F_8(H_2O)_2$, in which the Jahn–Teller distortion of Cu^{2+} octahedra is expected to influence the superexchange Fe—F—Cu angles and therefore the magnetic properties.

Experimental. Hydrothermal growth from CuF_2 and FeF_3 in 40% HF, 743 K, 185 MPa, 5*M* NaF solution, $(NaF/CuF_2/FeF_3) = (1/1/2)$. Prismatic light-green crystal 0·05 × 0·04 × 0·14 mm. Data collected on a Siemens AED-2 four-circle diffractometer, ω–2θ step scan mode in N steps of $\Delta\omega°$, $37 \leq N \leq 50$, $0{\cdot}023 \leq \Delta\omega \leq 0{\cdot}027$. Time per step: 2 s. Profile-fitting data analysis (Clegg, 1981); isotropic linewidth $\omega = (0{\cdot}85 + 0{\cdot}05\tan\theta)°$. Aperture $D = 4{\cdot}0$ mm. Lattice constants based on 24 reflections at $2\theta \simeq 30°$. Absorption correction by the Gauss method, $A_{\max} = 0{\cdot}76$, $A_{\min} = 0{\cdot}64$. Intensity measurement of one independent set to $2\theta_{\max} = 90°$ within the range $-14 \leq h \leq 14$, $0 \leq k \leq 14$, $0 \leq l \leq 25$. Standard reflections 400, 008, $0\bar{4}1$, intensity variation 1·0%, 3478 reflections measured, 2321 independent reflections used for refinements $[|F| > 6\sigma(|F|)]$. Structure solved from Patterson interpretation with *SHELXS*86 program (Sheldrick, 1985). F magnitudes used in least-squares refinements: 70 parameters refined; mean $\Delta/\sigma = 0{\cdot}007$, max. $\Delta/\sigma = 0{\cdot}070$; secondary-extinction factor: $x = 1{\cdot}6\,(2) \times 10^{-7}$; atomic scattering factors for H, O, F, Fe, Cu from *International Tables for X-ray Crystallography* (1974); calculations with *SHELX*76 (Sheldrick, 1976) on a MicroVAX II computer. Patterson interpretation gives a solution with two metallic atoms. Then, refinements of atomic positions and isotropic thermal motion, followed by Fourier or difference Fourier maps, lead to the localization of all non-H atoms ($R = 0{\cdot}075$). The residual decreases to $R = 0{\cdot}037$ when refining the anisotropic thermal parameters. Positions of H atoms in two

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

	x	y	z	B_{eq}
Cu	$\frac{1}{4}$	$\frac{1}{4}$	0	1.14 (1)*
Fe	0·2500 (1)	0·0449 (1)	0·2526 (1)	0·64 (1)*
F(1)	0·3016 (2)	0·2964 (2)	0·2680 (1)	1·48 (5)*
F(2)	0·2536 (2)	0·0752 (2)	0·1065 (1)	1·64 (5)*
F(3)	0·2470 (2)	0·0243 (3)	0·3977 (1)	1·77 (5)*
F(4)	0	0·0987 (3)	$\frac{1}{4}$	1·67 (7)*
F(5)	0	0·4946 (3)	$\frac{1}{4}$	1·57 (7)*
O(*W*)	0·4934 (3)	0·2500 (3)	0·5014 (2)	2·95 (9)*
H(1)	0·420 (6)	0·170 (6)	0·461 (3)	2·0 (6)
H(2)	0·073 (6)	0·166 (6)	0·458 (3)	2·0 (6)

* $B_{eq} = (4/3)\sum_i\sum_j\beta_{ij}(\mathbf{a}_i.\mathbf{a}_j)$ (Hamilton, 1959).

Table 2. *Selected bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

2 × Cu—F(2)	1·909 (1)	Fe—F(1)	1·922 (1)
2 × Cu—F(3)	2·451 (2)	Fe—F(1′)	1·936 (1)
2 × Cu—O(*W*)	1·935 (2)	Fe—F(2)	1·917 (1)
		Fe—F(3)	1·897 (1)
		Fe—F(4)	1·928 (1)
		Fe—F(5)	1·923 (1)
			⟨d⟩ = 1·921
O(*W*)—H(1)	0·97 (5)		
O(*W*)—H(2)	0·96 (5)		
F(3)—H(1)	1·89 (5)		
F(3)—H(2)	1·87 (5)		
H(1)—H(2)	1·64 (9)		
Fe—F(2)—Cu	143·4 (1)	O(*W*)—H(1)—F(3)	171 (4)
Fe—F(3)—Cu	127·6 (1)	O(*W*)—H(2)—F(3)	166 (5)
Fe—F(1)—Fe	152·8 (1)	H(1)—O(*W*)—H(2)	114 (4)
Fe—F(4)—Fe	155·8 (1)		
Fe—F(5)—Fe	157·4 (1)		

Table 3. *Valence-bond analysis of* $CuFe_2F_8(H_2O)_2$ *using the Zachariasen law for metal—anion bonds and the Brown–Shannon law for* O—H

	Cu	Fe	H(1)	H(2)	Σ	$\Sigma_{expected}$
F(1)		$0·51^a$ $0·49^a$			1·00	1
F(2)	$0·45^a$ $0·45^a$	$0·51^a$			0·96	1
F(3)	$0·10^a$ $0·10^a$	$0·54^a$	$[0·20]^c$	$[0·20]^c$	1·04	1
F(4)		$0·50\ (\times 2)^a$			1·00	1
F(5)		$0·50\ (\times 2)^a$			1·00	1
O(*W*)	$0·49^a$		$0·80^b$	$0·80^b$	2·09	3
Σ	2·08	3·05	1	1		
$\Sigma_{expected}$	2	3	1	1		

(*a*) $s = 0·333\exp[-(2·023 - d_i)/0·37]$ for Cu—F (Pannetier, unpublished results), $s = 0·5\exp[-(1·927 - d_i)/0·37]$ for Fe—F (Pannetier, unpublished results), $s = \exp[-(d_i - 1·65)/0·40]$ for Cu—O (Brown, 1981). (*b*) $s = (d_i/0·87)^{2·2}$ for O—H (Brown, 1981). Owing to the large uncertainty in the observed O—H distance, the man value $d_{O—H} = 0·96$ Å was taken. (*c*) Values in square brackets correspond to the difference 1·00 − 0·80 (expected − calculated) since $s_{H—F}$ is not available.

8(*f*) sites were then found from a difference Fourier map calculated from data limited to $\sin\theta = 0·4$. Refinement of their atomic coordinates and isotropic thermal parameter (fixed equal for both positions) leads to a final $R = 0·036$, $wR = 0·040$, $w = 1·69/[\sigma^2(|F_o|) + 0·00039F_o^2]$. Max. and min. heights in final difference map 0·93 and −1·52 e Å^{-3}.

Discussion. The final atomic coordinates and thermal parameters are given in Table 1.* Characteristic interatomic distances and angles are listed in Table 2. The structure, presented in Fig. 1, is very similar to that of $Fe_3F_8(H_2O)_2$ ($a' \simeq b' \simeq c' \simeq 7·5$ Å, $\beta \simeq 120°$) with the cell relationships: $a \simeq a'$, $b \simeq b'$, $c \simeq 0·5 \times (-a' + c')$. A cationic order arises between Fe^{3+} and Cu^{2+}: layers of corner-sharing FeF_6 octahedra (at $z = \frac{1}{4}$ and $\frac{3}{4}$) are bonded by copper polyhedra. The mean Fe—F distance (Table 2) corresponds to the sum of the ionic radii of Fe^{3+} (0·645 Å) and F^- (1·285 Å). Owing to the Jahn–Teller effect, the $CuF_4(H_2O)_2$ octahedra are strongly elongated: they present two short Cu—F(2) distances [$d = 1·909$ (1) Å], two short Cu—O(*W*) distances [$d = 1·935$ (2) Å] and two long Cu—F distances [$d = 2·451$ (2) Å]. A valence-bond analysis (Table 3) shows that the four short distances correspond to 90% of the bond strength s given by Cu^{2+}. So, the coordination of copper can also be described as a $CuF_2(H_2O)_2$ square plane. Indeed, the F(3) atoms, which correspond to the long Cu—F distances, are mainly bonded [90% of the bond strength of F(3)] to Fe^{3+} and H atoms [$d_{H\cdots F} = 1·88$ (5) Å] of the water molecules [$d_{O—H} = 0·96$ (5) Å]. Such typical distances have already been encountered in $CuF_2.4H_2O$ (Abrahams & Prince, 1962) and $CuWO_3F_2$ (Moutou, Francisco, Chaminade, Pouchard & Hagenmuller, 1986). The superexchange angles are about 155° for Fe—F—Fe but

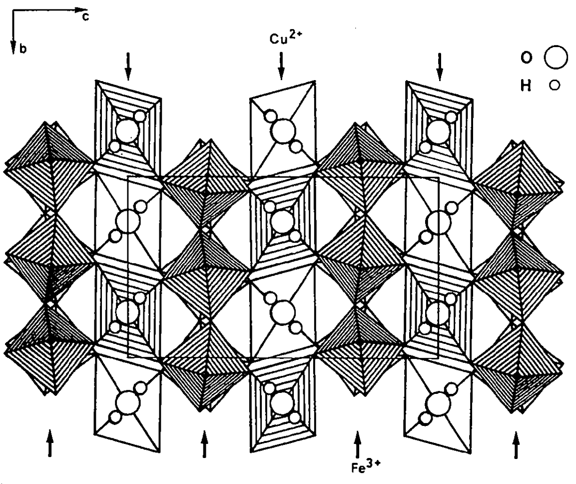

Fig. 1. (010) projection of the structure. Hatched Cu^{2+} polyhedra lie at $x = \frac{3}{4}$.

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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 52118 (16 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

decrease to 143·4 (1)° for Fe—F(2)—Cu and 127·6 (1)° for Fe—F(3)—Cu. It is expected that the magnetic coupling constant $J_{\text{Fe—F—Cu}}$ could be weak compared with $J_{\text{Fe—F—Fe}}$ and could lead to interesting magnetic properties. A study of these properties is currently in progress.

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Room-Temperature Structures of Oxocopper(II) Vanadate(V) Hydrates, $Cu_3V_2O_8(H_2O)$ and $CuV_2O_6(H_2O)_2$

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Abstract. $Cu_3V_2O_8(H_2O)$, $M_r = 438{\cdot}51$, monoclinic, $P2_1/m$, $a = 7{\cdot}444\,(1)$, $b = 6{\cdot}658\,(1)$, $c = 7{\cdot}759\,(1)$ Å, $\beta = 93{\cdot}57\,(1)°$, $V = 383{\cdot}8\,(2)$ Å^3, $Z = 2$, $D_x = 3{\cdot}20$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 10{\cdot}5$ mm^{-1}, $F(000) = 414{\cdot}0$, $R = 0{\cdot}047$ for 1307 unique reflections. $CuV_2O_6(H_2O)_2$, $M_r = 297{\cdot}47$, monoclinic, $P2/c$, $a = 5{\cdot}617\,(1)$, $b = 5{\cdot}595\,(1)$, $c = 11{\cdot}333\,(2)$ Å, $\beta = 91{\cdot}04\,(1)°$, $V = 356{\cdot}1\,(2)$ Å^3, $Z = 2$, $D_x = 2{\cdot}77$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 5{\cdot}4$ mm^{-1}, $F(000) = 286$, $R = 0{\cdot}045$ for 1355 unique reflections. Crystal hydrothermal growth was from Cu_2O and NH_4VO_3 in a 2·5 *M* NH_4HF_2 solution. In $Cu_3V_2O_8(H_2O)$, copper atoms adopt either a square planar or a fivefold prismatic coordination. Dimeric entities are formed by edge sharing CuO_5 and $CuO_4(H_2O)$ polyhedra. These groups are linked by CuO_4 square planes and by pyrovanadate $(V_2O_7)^{4-}$ di-tetrahedra. The structure of $CuV_2O_6(H_2O)_2$ consists of infinite chains of $[VO_{3/2}O]_{2n}$ tetrahedra connected by isolated $CuO_{2/2}(H_2O)_2$ square planes. In both structures, the location of the oxygen of water molecules can be predicted by valence bond analysis.

Introduction. As part of a general study concerning the hydrothermal synthesis of minerals and their by-products potentially interesting for their magnetic or electric properties, we focused our attention on several copper vanadates, hydrated [$Cu_3V_2O_8.3H_2O$: volborthite (Struppler, 1965; Leonardsen & Petersen, 1974)] or anhydrous [$Cu_3V_2O_8$: macbirneyite (Hughes, Christian, Finger & Malinconico, 1987)].

Hydrothermal growth of these copper vanadates was performed at low temperature (493 K) in ammonium fluoride solution. A new compound $Cu_3V_2O_8(H_2O)$ resulted as the major constituent and a small amount of dark green crystals of $CuV_2O_6(H_2O)_2$ was also produced. Powder samples of this last compound had already been prepared by crystallization from a solution of copper sulfate and ammonium or sodium vanadate (Fleury, 1966).

The structures of $Cu_3V_2O_8(H_2O)$ and $CuV_2O_6(H_2O)_2$ are established by X-ray single-crystal diffraction and presented here.

Experimental. Hydrothermal growth in a Teflon digestion autoclave, from Cu_2O and NH_4VO_3 in 2·5 *M* NH_4HF_2 solution, 493 K, 36 h. Data collected on a Siemens AED2 four-circle diffractometer, profile-fitting data analysis (Clegg, 1981). Structures solved from direct methods with Tang option of *SHELX76* program (Sheldrick, 1976). *F* magnitudes used in least-squares refinements. Hydrogen atoms were not located. Atomic scattering factors for O, Cu and V from *International Tables for X-ray Crystallography* (1974); calculations with *SHELX76* program (Sheldrick, 1976) on a MicroVAX II computer.

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