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 $J_{Fe—F—Cu}$ could be weak compared with $J_{Fe—F—Fe}$ 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. $Cu_3V_2O_8(H_2O)$, $M_r = 438·51$, monoclinic, $P2_1/m$, $a = 7·444$ (1), $b = 6·658$ (1), $c = 7·759$ (1) Å, $\beta = 93·57$ (1)°, $V = 383·8$ (2) Å^3, $Z = 2$, $D_x = 3·20$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 10·5$ mm^{-1}, $F(000) = 414·0$, $R = 0·047$ for 1307 unique reflections. $CuV_2O_6(H_2O)_2$, $M_r = 297·47$, monoclinic, $P2/c$, $a = 5·617$ (1), $b = 5·595$ (1), $c = 11·333$ (2) Å, $\beta = 91·04$ (1)°, $V = 356·1$ (2) Å^3, $Z = 2$, $D_x = 2·77$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å, $\mu = 5·4$ mm^{-1}, $F(000) = 286$, $R = 0·045$ 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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Table 1. *Coordinates and equivalent isotropic temperature factors* ($Å^2$) *in* $Cu_3V_2O_8(H_2O)$ *and* $CuV_2O_6(H_2O)_2$, *with e.s.d.'s in parentheses*

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

	x	y	z	B_{eq}
$Cu_3V_2O_8(H_2O)$				
Cu(1)	0	0	0	0·75 (3)
Cu(2)	0·1625 (1)	0·25	0·7041 (1)	0·76 (3)
Cu(3)	0·3237 (1)	0·25	0·0703 (1)	0·87 (3)
V(1)	0·6613 (1)	0·25	0·7841 (1)	0·56 (3)
V(2)	0·7332 (2)	0·25	0·3335 (1)	0·62 (3)
O(1)	0·0962 (6)	0·25	−0·0595 (6)	0·7 (2)
O(2)	0·2382 (5)	−0·0370 (6)	0·1297 (5)	1·1 (1)
O(3)	0·4465 (7)	0·25	0·8263 (7)	1·2 (2)
O(4)	0·8613 (5)	0·4542 (6)	0·2960 (5)	1·2 (2)
O(5)	0·5396 (7)	0·25	0·2142 (8)	1·7 (2)
O(6)	0·6803 (9)	0·25	−0·4425 (8)	1·8 (3)
O(*w*)	0·212 (1)	0·25	0·4576 (9)	1·9 (3)
$CuV_2O_6(H_2O)_2$				
Cu	0	0	0	1·82 (3)
V	0·2350 (1)	0·4519 (1)	0·1620 (1)	1·13 (2)
O(1)	0	0·5664 (8)	0·2500 (0)	2·0 (2)
O(2)	0·1830 (6)	0·1667 (5)	0·1272 (3)	2·0 (1)
O(3)	0·5	0·4746 (8)	0·25	2·2 (2)
O(4)	0·2528 (6)	0·6146 (6)	0·0456 (3)	2·4 (2)
O(*w*)	0·2612 (7)	0·0615 (7)	−0·1118 (3)	3·1 (2)

Table 2. *Selected bond lengths* (Å) *and angles* (°) *in* $Cu_3V_2O_8(H_2O)$ *and* $CuV_2O_6(H_2O)_2$, *with e.s.d's in parentheses*

$Cu_3V_2O_8(H_2O)$			
2 × Cu(1)—O(1)	1·881 (2)	Cu(2)—O(1)	1·929 (5)
2 × Cu(1)—O(2)	1·999 (4)	Cu(2)—O(3)	2·263 (6)
	⟨*d*⟩ = 1·940	2 × Cu(2)—O(4)	1·977 (6)
		Cu(2)—O(*w*)	1·970 (6)
2 × Cu(1)—O(4)	2·594 (6)		⟨*d*⟩ = 2·023
Cu(3)—O(1)		1·916 (5)	
2 × Cu(3)—O(2)		2·075 (4)	
Cu(3)—O(3)		2·153 (5)	
Cu(3)—O(5)		1·899 (6)	
		⟨*d*⟩ = 2·024	
2 × V(1)—O(2)	1·719 (6)	2 × V(2)—O(4)	1·696 (4)
V(1)—O(3)	1·652 (5)	V(2)—O(5)	1·664 (6)
V(1)—O(6)	1·773 (6)	V(2)—O(6)	1·806 (5)
	⟨*d*⟩ = 1·716		⟨*d*⟩ = 1·715
$CuV_2O_6(H_2O)_2$			
2 × Cu—O(2)	1·988 (3)	V—O(1)	1·788 (2)
2 × Cu—O(*w*)	1·986 (4)	V—O(2)	1·668 (3)
	⟨*d*⟩ = 1·987	V—O(3)	1·781 (1)
		V—O(4)	1·607 (3)
2 × Cu—O(4)	2·628 (5)		⟨*d*⟩ = 1·711
V—O(1)—V	138·0 (8)	V—O(3)—V	171·8 (8)
Cu—O(4)—V	125·8 (8)	Cu—O(2)—V	134·9 (8)

$Cu_3V_2O_8(H_2O)$: metallic black tabular crystal 0·022 × 0·054 × 0·15 mm. ω–2θ step-scan mode in N steps of $\Delta\omega$°, $37 \le N \le 45$, $0·025 \le \Delta\omega \le 0·068$; time per step: 2 s. Isotropic linewidth $\omega = (1·000 + 0·103\tan\theta)$°. Aperture $D = 4·0$ mm. Lattice constants based on 30 reflections measured in double step scan mode at $\pm 2\theta \simeq 30$°; absorption correction by the Gauss method, $A_{max} = 0·79$, $A_{min} = 0·54$. Intensity measurement of one independent set to $2\theta \le 70$° within ranges $-12 \le h \le 12$, $0 \le k \le 12$, $0 \le l \le 12$. Standard reflections 012, $\bar{4}12$, 013, intensity variation 0·7%, 1811 reflections measured, 1307 independent reflections used for refinements $[|F| > 6\sigma(|F|)]$. 80 parameters refined; mean $\Delta/\sigma = 0·0034$, max. $\Delta/\sigma = 0·009$; secondary-extinction factor: $x = 2·1\,(8) \times 10^{-7}$. A solution with five metallic atoms in 2(*a*) and 2(*e*) special positions was found with the multisolution tangent direct method of *SHELX*76. Successive refinements and Fourier maps located the oxygen atoms ($R = 0·073$). Further refinements of anisotropic thermal parameters led to $R = 0·047$, $wR = 0·050$. Max. and min. heights in final difference F map: $+2·8$ and $-2·4$ e Å^{-3}. $w = 1·32/[\sigma^2(|F_o|) + 0·0015F_o^2]$.

$CuV_2O_6(H_2O)_2$: dark green prismatic crystal 0·045 × 0·080 × 0·060 mm. ω–2θ step-scan mode in N steps of $\Delta\omega$°, $37 \le N \le 45$, $0·025 \le \Delta\omega \le 0·027$; time per step: 2 s. Isotropic line width $\omega = (0·930 + 0·044\tan\theta)$°. Aperture $D = 4·0$ mm. Lattice constants based on 28 reflections measured in double step scan mode at $\pm 2\theta \simeq 30$°; absorption correction by the Gauss method, $A_{max} = 0·82$, $A_{min} = 0·60$. Intensity measurement to $2\theta \le 70$° of two independent sets within ranges $-8 \le h \le 9$, $0 \le |k| \le 9$, $0 \le l \le 18$. Standard reflections 124, 032, $\bar{3}0\bar{2}$, intensity variation 1·2%, 3408 reflections measured, 1355 independent reflections used for refinements $[|F| > 6\sigma(|F|)]$, $R_{int} = 0·028$. 54 parameters refined; max. $\Delta/\sigma = 0·001$; secondary-extinction factor: $x = 1·6 \times 10^{-7}$. Multisolution tangent direct method of *SHELX*76 gives a solution with two metallic atoms. Successive refinements and Fourier maps allowed differentiation between copper and vanadium atoms and location of oxygen atoms ($R = 0·102$). The residual decreases to $R = 0·045$, $wR = 0·043$ when refining the anisotropic thermal parameters. Max. and min. heights in final difference F map: 1·35 and $-1·70$ e Å^{-3}. $w = 3·31/[\sigma^2(|F_o|) + 0·00002F_o^2]$.

Discussion. The final atomic coordinates and equivalent isotropic temperature factors are listed in Table 1.* Characteristic interatomic distances and selected angles are given in Table 2.

$Cu_3V_2O_8(H_2O)$: vanadium atoms adopt a tetrahedral coordination while copper atoms are either in a square plane [Cu(1)] or fivefold coordination [Cu(2) and Cu(3)] (Fig. 1). Both Cu(2) and Cu(3) polyhedra are very close to square pyramids but their nature is different. A valence bond analysis (Table 3)

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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 52135 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Valence bond analysis of* $Cu_3V_2O_8(H_2O)$ *and* $CuV_2O_6(H_2O)_2$

The Zachariasen law* is used for Cu—O bonds and the Shannon–Calvo law† for V—O.

$Cu_3V_2O_8(H_2O)$

	O(1)	O(2)	O(3)	O(4)	O(5)	O(6)	O(*w*)	Σs
V(1)		2 × 1·22	1·50			1·05		4·99
V(2)				1·31	1·45	0·95		5·02
Cu(1)	2 × 0·56	2 × 0·42		2 × 0·09				2·14
Cu(2)	0·50		0·22	2 × 0·44			0·45	2·05
Cu(3)	0·51	0·34	0·28		0·55			2·04
Σs	2·13	1·98	2·00	1·84	2·00	2·00	0·45	
$2-\Sigma s$	+0·13	−0·02	0·00	−0·16	0·00	0·00	+1·55	

$CuV_2O_6(H_2O)_2$

	O(1)	O(2)	O(3)	O(4)	O(*w*)	Σs
V	1·01	1·43	1·02	1·74		5·20
Cu		2 × 0·43		2 × 0·09	2 × 0·43	1·90
Σs	2·02	1·86	2·04	1·83	0·43	
$2-\Sigma s$	−0·02	+0·14	−0·04	+0·17	1·57	

*$s = \exp[-(d_i - 1{\cdot}65)/0{\cdot}40]$.
†$s = 1{\cdot}25\,(1{\cdot}714/d_i)^{5{\cdot}1}$.

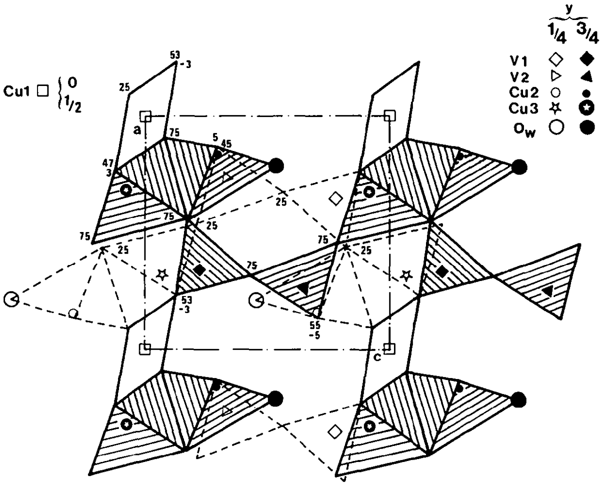

Fig. 1. (010) projection of the structure of $Cu_3V_2O_8(H_2O)$. Hatched polyhedra lie at $y = \frac{3}{4}$.

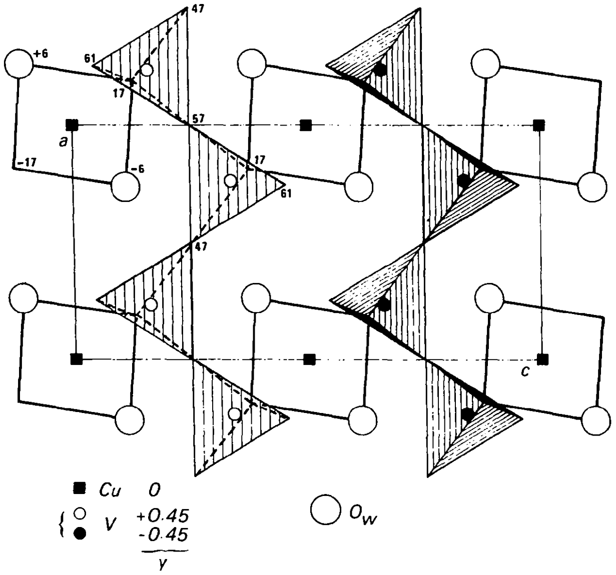

Fig. 2. (010) projection of the structure of $CuV_2O_6(H_2O)_2$ (heights of oxygen atoms along **b** are in hundreds).

shows two main features: (i) O(4) does not partake to a noticeable extent in the coordination of Cu(1) which is therefore fourfold coordinated, (ii) oxygen atom O(*w*) receives only 0·45 valence unit (v.u.) from Cu(2), whereas the bond strength of all the oxygen atoms is nearly fulfilled. This means that O(*w*) corresponds to a water molecule. Therefore, Cu(2) and Cu(3) form $CuO_4(H_2O)$ and CuO_5 polyhedra, respectively. Both the Cu(2) coordination and the connection of Cu(2) and Cu(3) polyhedra are rather sparse. Cu(2) and Cu(3) pyramids share lateral edges, instead of basal edges as is usually found. The dimeric Cu(2)–Cu(3) entities are linked to each other along **b** by infinite corner sharing *trans*-chains of Cu(1) square planes. These chains share two opposite edges with Cu(3) pyramids. Isolated pyrovanadate groups $(V_2O_7)^{4-}$ at $y = \frac{1}{4}$ and $y = \frac{3}{4}$ ensure the connection of these complex chains *via* corners. The corresponding framework leaves vacancies where hydrogen atoms of water molecules can reside. It is also clear from the valence bond analysis that hydrogen bonds, if any, can only occur with O(4).

$CuV_2O_6(H_2O)_2$: the structure (Fig. 2) can be described as infinite *cis*-chains of $[VO_{4/2}]_{2n}^{2n+}$ tetrahedra running along **a**. These chains are connected together by distorted $[CuO_{4/2}(H_2O)_2]^{2-}$ octahedra in order to build up the three-dimensional network. Valence bond analysis (Brown, 1981) of the structure (Table 3) clearly shows that water molecules correspond to O(*w*). Indeed, the bond strength *s* given by

Cu to O(*w*) is close to 0·4 v.u. In order to saturate its bond strength to 2·0 v.u., O(*w*) must receive 1·6 v.u., *i.e.* twice the common value (0·8 v.u.) given by H in water molecules. The Jahn–Teller effect on copper leads to four short distances in a square plane $CuO_2(H_2O)_2$. Two long Cu—O distances correspond to less than 16% of the bond strength given by Cu^{2+}. Valence bond calculations also show that hydrogen of water molecules form weak hydrogen bonds with O(2) and O(4). These two latter atoms do not saturate their bond strength, at variance with O(1) and O(3).

From these structural studies, $Cu_3V_2O_8(H_2O)$ appears to be a basic copper pyrovanadate monohydrate, whereas $CuV_2O_6(H_2O)_2$ is a copper metavanadate dihydrate. It is to be noted that the structure of $Cu_3V_2O_8(H_2O)$ differs from that of the isoformula phosphate $Cu_3P_2O_8(H_2O)$ (Riou, Gerault & Cudennec, 1985). Now, it will be interesting to study the thermal dehydration of these copper vanadates and to analyse the structure of the corresponding anhydrous compounds.

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Structures of Two Disulfide-Bridged Compounds

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Abstract. Bis(tetraphenylarsonium) *cis,cis*-1,2,5,6-tetracyano-3,4-dithiahexa-1,5-diene-1,6-dithiolate, $[As(C_6H_5)_4]_2C_8N_4S_4$, (1); $M_r = 1047{\cdot}0$, monoclinic, $P2/n$, $a = 13{\cdot}692\,(3)$, $b = 9{\cdot}647\,(3)$, $c = 19{\cdot}872\,(5)$ Å, $\beta = 102{\cdot}71\,(2)^\circ$, $U = 2560{\cdot}5\,(1{\cdot}0)$ Å^3, $Z = 2$, $D_x = 1{\cdot}36$ g cm^{-3}, $\mu(\text{Mo } K\alpha) = 14{\cdot}98$ cm^{-1}, $F(000) = 1068$, $R = 0{\cdot}046$ for 2514 observed reflections. 4,4′,6,6′-Tetramethyl-2,2′-thiopyrimidine, $C_{12}H_{14}N_4S_2$, (2); $M_r = 278{\cdot}4$, monoclinic, $P2_1/c$, $a = 13{\cdot}273\,(3)$, $b = 9{\cdot}075\,(4)$, $c = 12{\cdot}281\,(4)$ Å, $\beta = 107{\cdot}66\,(2)^\circ$, $U = 1409{\cdot}7\,(7)$ Å^3, $Z = 4$, $D_x = 1{\cdot}31$ g cm^{-3}, $\mu(\text{Mo } K\alpha) = 3{\cdot}49$ cm^{-1}, $F(000) = 584$, $R = 0{\cdot}054$ for 1554 observed reflections. Both compounds were produced by oxidation of thiols by uranyl salts. Dimensions are normal, with C—S 1·759 (6) and 1·782 (4), S—S 2·051 (3) and 2·021 (2) Å respectively, and torsion angles C—S—S—C of 82·7 (4) and 95·7 (4)°.

Introduction. During our studies of compounds containing U—S bonds (Alcock & Pennington, 1989), we investigated the reactions of thiolate anions with uranyl salts. We were unsuccessful in isolating the intended complexes (even though one had previously been reported), because of the production of compounds containing S—S bonds formed by the oxidation of the ligand. The structures of two such compounds are described here.

Experimental. *Preparation.* (1) was isolated during an attempt to prepare the 1,2-dicyanoethylene-1,2-dithiol salt of uranium(VI). The thiol ligand was prepared using the method described by Davison & Holm (1967). 0·50 g of this ligand in methanol was then added to a solution of uranyl acetate (0·58 g) producing an olive-green-coloured solution. When addition was complete, the mixture was heated at reflux for 2 h. When cool, the volume of solvent was reduced until the first sign of precipitation. The solution was then filtered and tetraphenylarsonium chloride (1·0 g) in methanol added. After further cooling, yellow needle-like crystals had formed, which were shown by structure determination to be the *cis,cis*-disulfide.

Dimethylthiopyrimidine dimer (2), was formed in an attempt to prepare the dimethylthiopyrimidine product of uranyl nitrate described by Baghlaf,

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