α Cupric Divanadate

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Abstract. $\alpha Cu_2V_2O_7$, orthorhombic, *Fdd*2, $a = 20\cdot645$ (20), $b = 8\cdot383$ (7), $c = 6\cdot442$ (12) Å, $Z = 8$, $D_{exp} = 3\cdot969$, $D_x = 3\cdot94$ g cm^{-3}. Crystals were grown from a melt under O_2 atmosphere. The anion, V_2O_7, contains a crystallographic twofold axis through the bridging oxygen atom with V–O bond lengths ranging from $1\cdot648$ (5) to $1\cdot743$ (2) Å and a V–O–V angle of $147\cdot8$ (5)°. Cu^{2+} is bonded strongly to four oxygen atoms with Cu–O bond lengths ranging from $1\cdot880$ (5) to $1\cdot972$ (5) Å and weakly to a fifth at $2\cdot542$ (4) Å.

Introduction. The structure of $\alpha Cu_2V_2O_7$ (Mercurio-Lavaud & Frit, 1973*a*) appeared after the completion of the present study. Since our refinement of this structure is more precise, if not more accurate, its publication seemed advisable.

Considerable interest has been generated in the study of the structures of the $M_2X_2O_7$ series of compounds. The lattice parameters of all the divanadates for which single-crystal data, but not necessarily structures, are available are listed in Table 1. Surprisingly, a large number of unique structure types are found. The structure of the high-temperature form (β) of $Cu_2V_2O_7$ (Mercurio-Lavaud & Frit, 1973*b*) is isostructural with that of $\alpha Zn_2V_2O_7$ (Gopal & Calvo, 1973). The nature of α to β transition in $Cu_2V_2O_7$ is of considerable interest since the α form has not appeared previously in any related system.

The intensities and cell dimensions were obtained from a cubically shaped crystal with 0·05 mm as the average dimension. A Syntex $P\bar{1}$ automatic diffrac-

tometer was used (Mo $K\alpha$, graphite monochromatized, θ–2θ scan with variable scan rate, scintillation counter with pulse-height discrimination, a standard reflexion measured at intervals of 50 reflexions and backgrounds determined 1° from either side of the peak). Data were collected for a quadrant up to 2θ of 50°, yielding a total of 488 symmetry-independent reflexions with intensities of positive measure and 28 unobserved (I between 0 and 3σ). The systematic absences are hkl in general if either $h+k$ or $k+l$ is odd, for $0kl$ if $k+l = 4n$ and $h0l$ if $h+l = 4n$. The data were corrected for Lorentz, polarization, absorption and extinction effects.

The structure was determined from the Patterson function. Full-matrix least-squares refinement with individual atomic anisotropic thermal parameters and weights, $\omega = [7\cdot5 + 0\cdot25F_o + 0\cdot005F_o^2]^{-1}$ chosen so that $\omega(|F_o| - |F_c|)^2$ would be independent of F_o, resulted in a final R value of 0·028.* The atomic parameters are in Table 2 and the thermal parameters in Table 3. The pertinent bond lengths and angles are in Table 4.

Discussion. The present refinement of the structure of $\alpha Cu_2V_2O_7$ does not differ significantly from that reported by Mercurio-Lavaud & Frit (1973*a*). However, the standard errors are smaller by a factor of about ten. This allows a more detailed comparison of

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Table 1. *Unit-cell parameters for* $M_2V_2O_7$ *structures*

	a (Å)	b (Å)	c (Å)	$\alpha(°)$	$\beta(°)$	$\gamma(°)$	Space group
$Mg_2V_2O_7{}^a$	5·421	4·937	10·750	99·49	75·17	81·29	$P\bar{1}$
$Co_2V_2O_7{}^b$	6·594	8·370	9·470		100·17		$P2_1/c$
$Ni_2V_2O_7{}^b$	6·504	8·298	9·351		100·03		$P2_1/c$
$Zn_2V_2O_7{}^c$	7·429	8·340	10·098		111·37		$C2/c$
$\alpha Cu_2V_2O_7$	20·645	8·383	6·442				Fdd2
$\beta Cu_2V_2O_7{}^d$	7·685	8·007	10·09		110·27		$C2/c$
$Mn_2V_2O_7{}^e$	6·710	8·726	4·970		103·57		$C2/m$
$Cd_2V_2O_7{}^f$	7·088	9·091	4·963		103·33		$C2/m$
$Ca_2V_2O_7{}^g$	7·240	6·663	6·913	96·35	87·68	119·55	$P\bar{1}$
$Pb_2V_2O_7{}^h$	13·389	7·1616	7·1027		109·93		$P2_1/a$
$Sr_2V_2O_7{}^i$	7·055	7·055	25·642				$P4_1$
$\alpha Hg_2V_2O_7{}^j$	7·165	3·636	21·51				$Pnma$
$Ba_2V_2O_7{}^k$	13·571	7·320	7·306	90·09	99·48	87·32	$P\bar{1}$

References:

a Gopal & Calvo (1974). *b* Sauerbrei, Faggiani & Calvo (1974). *c* Gopal & Calvo (1973). *d* Mercurio-Lavaud & Frit (1973*b*). *e* Dorm & Marinder (1967). *f* Au & Calvo (1967). *g* Manolescu (1974). *h* Shannon & Calvo (1973). *i* Baglio & Dann (1971). *j* Quarton, Angenault & Rimsky (1973). *k* Hawthorne & Calvo (1975).

Table 2. *Atomic positions in* $\alpha Cu_2V_2O_7$

		x	y	z
Cu	16(b)	0·16580 (4)	0·36460 (9)	$\frac{3}{4}$
V	16(b)	0·19906 (4)	0·4054 (1)	0·2343 (2)
O(2)	16(b)	0·2453 (2)	0·5622 (6)	0·2774 (8)
O(3)	16(b)	0·1446 (2)	0·4368 (5)	0·0332 (7)
O(4)	16(b)	0·1619 (2)	0·3477 (5)	0·4592 (8)
O(1)	8(a)	$\frac{1}{4}$	$\frac{1}{4}$	0·1592 (12)

the effect of the environment on the bond lengths. The V–O(1) and V–O(3) bond lengths are the same length despite the fact O(1) is the bridging oxygen atom in the divanadate group. The V–O(2) bond is the shortest and the V–O(4) bond is of intermediate length. This trend is expected since O(3) is bonded strongly to two Cu ions, O(2) to one and O(4) is bonded strongly to one and weakly to another Cu ion.

The Cu ion shows fivefold coordination to oxygen atoms with the sixth oxygen atom over 3 Å from the Cu. The Cu–O bonds of intermediate length, lying between 1·943 and 1·972 Å, are significantly different in the present study. The shortest Cu–O bond is *trans* to the empty sixth site in the coordination sphere about Cu.

The relationship between the α and $\beta Cu_2V_2O_7$ structures is a curious one. Each structure contains sheets of V_2O_7 groups with a staggered configuration and lying on a crystallographic twofold axis (Fig. 1). Adjacent anions in the sheet are generated by C centring. The anions in a given sheet in $\alpha Cu_2V_2O_7$ must be rotated by 25°, about the twofold axes, towards the plane of the sheet (the bc plane). Those in the next adjacent sheet must be inverted about the V–V vector before the rotation in order to generate the anion packing of $\beta Cu_2V_2O_7$. After such changes the structure will have a monoclinic cell defined by b, c and

$\frac{1}{2}(a+b)$, in terms of the unit cell of $\alpha Cu_2V_2O_7$, whose dimensions ($a'=8·411$, $b'=6·448$, $c'=11·140$ Å and $\beta=112·1°$) are roughly as in $\beta Cu_2V_2O_7$. Finally, adjacent sheets must slip alternately by about $+c/8$ and $-c/8$ in order to accommodate the changed bonding environment of the Cu ions. Each Cu ion must break and reform at least three Cu–O bonds through the transition. These changes seem large for a reversible transformation.
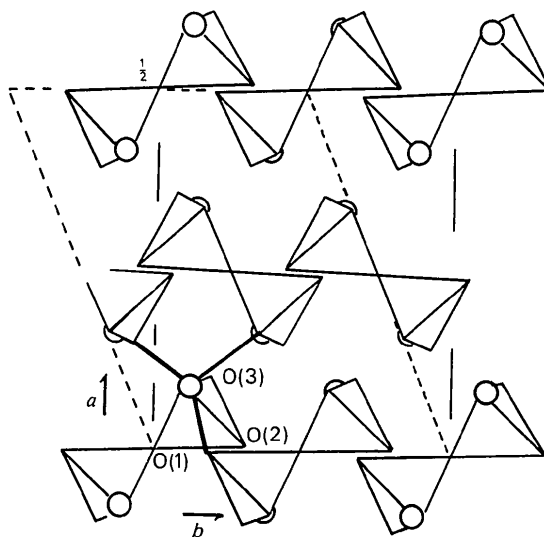

Fig. 1. Structure of $Cu_2V_2O_7$ projected on the ab plane. The anions, V_2O_7, are represented by edge-shared tetrahedra and the Cu ions by circles. Three bonds are shown to one of the copper ions. The remaining bonds are to O(1) directly below the copper ion and O(3) from the next cell along the c axis. The dashed lines outline the $\beta Cu_2V_2O_7$ cell.

Table 3. *Thermal parameters* ($\times 10^3$) *for atoms in* $Cu_2V_2O_7$

$U_{ij}=(2\pi b_i b_j)^{-1}\beta_{ij}$. The β_{ij} appear in the structure factor as exp $[-(\beta_{11}h^2+\ldots+2\beta_{12}hk+\ldots)]$ and the b_i's are reciprocal-lattice parameters.

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	18·4 (3)	26·5 (4)	5·8 (3)	12·0 (3)	−3·2 (3)	−4·6 (3)
V	3·9 (3)	10·1 (4)	1·1 (3)	−0·1 (3)	0·1 (3)	0·3 (4)
O(2)	15·0 (2)	34·0 (2)	13·0 (2)	13·0 (2)	−1·0 (2)	−1·0 (2)
O(3)	10·0 (1)	14·0 (2)	6·0 (2)	4·0 (1)	1·0 (1)	−4·0 (2)
O(4)	15·0 (2)	16·0 (2)	7·0 (2)	2·0 (1)	2·0 (2)	1·0 (2)
O(1)	29·0 (3)	42·0 (4)	14·0 (3)	−29·0 (3)		

Table 4. *Bond lengths* (Å) *and angles* (°) *in* $Cu_2V_2O_7$

Cu–O(4)^a	1·880 (5)	O(4)^a–Cu–O(4)^b	85·9 (2)	O(4)^b–Cu–O(2)^c	111·3 (2)
O(4)^b	2·542 (4)	O(2)^c	98·9 (2)	O(3)^a	73·7 (2)
O(2)^c	1·943 (5)	O(3)^d	159·3 (2)	O(3)^d	101·3 (2)
O(3)^a	1·972 (5)	O(3)^d	91·4 (2)	O(2)^c–Cu–O(3)^a	91·7 (2)
O(3)^d	1·955 (4)	O(3)^a–Cu–O(3)^d	89·5 (2)	O(3)^d	146·4 (2)
V–O(1)^a	1·743 (2)	O(1)^a–V–O(2)^a	107·0 (2)	O(2)^a–V–O(3)^a	112·4 (2)
O(2)^a	1·648 (5)	O(3)^a	107·3 (3)	O(4)^a	110·1 (2)
O(3)^a	1·736 (4)	O(4)^a	107·1 (3)	O(3)^a–V–O(4)^a	112·6 (2)
O(4)^a	1·709 (5)				
		V–O(1)–V′	147·8 (5)		

Symmetry transformations (exclusive of lattice translations): a x,y,z; b $\frac{1}{4}-x,\frac{1}{4}+y,\frac{1}{4}+z$; c $-x,\frac{1}{2}-y,\frac{1}{2}+z$; d $\frac{1}{4}-x,\frac{3}{4}+y,\frac{3}{4}+z$.

Table 5. V–O *bond lengths* (Å) *and* V–O–V *bond angles* (°) *in* $M_2V_2O_7$ *structures*

	$\langle V-O_t \rangle$	$\langle V-O_t \rangle$	V–O–V
$Mn_2V_2O_7{}^a$	1·69	1·760	180
$Cd_2V_2O_7{}^b$	1·692	1·757	180
$Zn_2V_2O_7{}^c$	1·697	1·751	151
$\beta Cu_2V_2O_7{}^{d*}$	1·693	1·770	
$\alpha Cu_2V_2O_7$	1·702	1·743	147·8
$Ba_2V_2O_7{}^e$	1·687	1·820	123·7
	1·688	1·823	125·6
$Sr_2V_2O_7{}^f$	1·69	1·81	122
	1·71	1·81	124
$Pb_2V_2O_7{}^g$	1·692	1·817	122
$Co_2V_2O_7{}^h$	1·694	1·849	117·6
$Ni_2V_2O_7{}^h$	1·692	1·846	117·1

a Dorm & Marinder (1967). *b* Au & Calvo (1967). *c* Gopal & Calvo (1973). *d* Mercurio-Lavaud & Frit (1973*b*). *e* Hawthorne & Calvo (1975). *f* Baglio & Dann (1971). *g* Shannon & Calvo (1973). *h* Sauerbrei, Faggiani & Calvo (1974).

* The table of atomic positions in this paper seems to contain errors. The values used here are those reported by these authors.

Table 5 summarizes the average bridging and terminal V–O bond lengths and V–O–V bond angles in the series of divalent metal ion divanadates. As the V–O–V angle increases the average bridging V–O bond length, $\langle V-O_b \rangle$, decreases. The average terminal V–O bond length shows no systematic variation. All anions with V–O–V bond angles of less than 148° have strong interactions between the divalent metal ion and the bridging oxygen atom. Therefore, these structures seem to fall into two groups based upon this characteristic. In the case of $Mg_2V_2O_7$ (Gopal & Calvo, 1974) one side of the anion has a long, but significant, interaction with a fifth oxygen atom (V–O = 2·440 Å).

Despite this, the structure is closely related to the thortvietite-like series of compounds. Many of these divalent metal ion divanadates show polymorphic transition. For example, Angenault (1970) has reported an orthorhombic phase of $Zn_2V_2O_7$ which is likely to be isotypic with that of $\alpha Cu_2V_2O_7$. Further studies of these polymorphs seems desirable.

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The Crystal Structure of Tetra-(4-methylphenyl)tin

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Abstract. $(4-CH_3C_6H_4)_4Sn$, tetragonal, $I\bar{4}$, $a = 13·819$ (8), $c = 6·406$ (4) Å, $Z = 2$, $D_c = 1·31$, $D_o = 1·32$ g cm^{-3} (by flotation in aqueous KI solution). The structure consists of discrete molecules which have crystallographic $\bar{4}$ symmetry. The methyl group is rigidly involved in the intermolecular structure. The final R value is 0·035.

Introduction. The title compound was prepared from the reaction of anhydrous tin tetrachloride and 4-methylphenylmagnesium bromide in ether/benzene solution. The purified compound was isolated from the crude reaction product by Soxhlet extraction and re-crystallized from benzene as long colorless glistening needles. From indexed Weissenberg photographs the systematic absences $h+k+l = 2n+1$ confirmed the body-centered tetragonal lattice found by Ismailzade & Zhdanov (1953). Cell parameters were determined by a least-squares refinement of the carefully measured angular settings of 12 reflections on a Picker FACS-1 automated diffractometer. The refined values given in the abstract compare with $a = 13·50$ and $c = 6·36$ Å reported by Ismailzade & Zhdanov (1953).

Three-dimensional intensity data were collected on the same diffractometer with zirconium-filtered Mo $K\alpha$ ($\lambda = 0·71069$ Å) radiation. The details of the data col-