pliquant bien pour celui-ci non pas un environnement octaédrique mais un environnement pyramidal à base carrée.

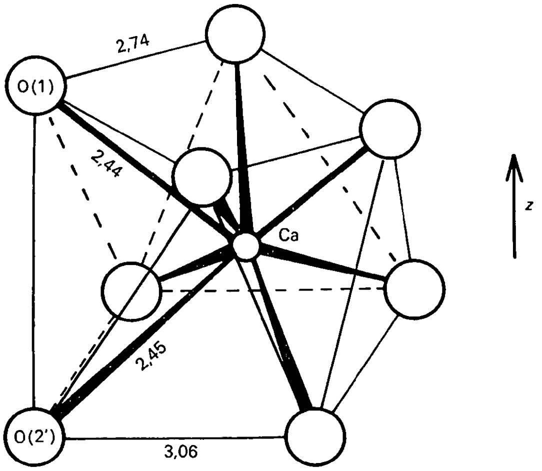

Fig. 2. Environnement oxygéné du calcium dans CaV_4O_9.

La coordinence du calcium est 8. Il s'insère entre les feuillets de composition $(V_4O_9)_n^{2n-}$. Les atomes d'oxygène liés au calcium se répartissent en nombre égal entre deux feuillets successifs; l'environnement oxygéné forme un antiprisme d'Archimède carré (Fig. 2).

Les distances Ca–O sont pratiquement égales (2,44 et 2,45 Å) mais sont légèrement supérieures à celles observées dans CaV_3O_7 où la coordinence du calcium était seulement [6+1].

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Crystal Structure of $Cu_5V_2O_{10}$

By R. D. Shannon* and C. Calvo

Institute for Materials Science, McMaster University Hamilton, Ontario, Canada

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$Cu_5V_2O_{10}$ is monoclinic with $a=8\cdot393$ (2), $b=6\cdot0652$ (8), $c=16\cdot156$ (3) Å, $\beta=108\cdot09$ (2)°, $Z=4$, and space group $P2_1/c$. The crystal structure was refined by full-matrix least-squares analysis to a $wR=0\cdot032$ using 1629 reflexions measured on a Syntex automatic diffractometer. The structure consists of a network made up of double chains of $Cu–O_6$ octahedra running parallel to **b** and chains formed from $Cu–O_6$ octahedra and $Cu–O_5$ trigonal bipyramids running parallel to **c**. These chains are linked to each other by edge sharing of the octahedra and trigonal bipyramids and corner sharing of the $V(2)O_4$ tetrahedra. Two such networks at $x\simeq\frac{1}{4}$ and $\frac{3}{4}$ are linked by the $V(1)O_4$ tetrahedra. Cu(1) and Cu(2) are octahedrally coordinated by oxygen atoms and show typical Jahn–Teller distortion. Cu(4) is also octahedrally coordinated but has an unusual distortion in which one equatorial and one apical, rather than 2 apical Cu–O bonds, are elongated. The mean Cu–O distances differ significantly for the three octahedra. These differences and those in other Cu-containing oxides are related to the degree of distortion of the octahedra. Cu(3) and Cu(5) are each surrounded by five oxygen atoms in the form of distorted trigonal bipyramids. The apical bonds are shorter than the equatorial bonds as in Cu_2OSO_4, $Cu_3As_2O_8$ and Cu_3WO_6. The differences in individual V–O distances are related to the bond-strength sums around the oxygen atoms.

Introduction

Brisi & Molinari (1958) and Fleury (1966, 1969) reported the synthesis of $Cu_5V_2O_{10}$, an incongruently melting compound in the $CuO–V_2O_5$ system. Fleury concluded from magnetic susceptibility measurements that $Cu_5V_2O_{10}$ contained divalent Cu but no structural information was given. We were interested in this compound in connexion with a study of interatomic distances in vanadates containing a large proportion of electronegative ions, *e.g.* compounds such as $Cu_3V_2O_8$ (Shannon & Calvo, 1972) and $Pb_2V_2O_7$ (Shannon & Calvo, 1973*a*). In this paper we report the single crystal synthesis and structure refinement of $Cu_5V_2O_{10}$.

Experiments

Crystals of $Cu_5V_2O_{10}$ were grown from a KVO_3 melt. Starting materials were reagent grade CuO, V_2O_5 and K_2CO_3. A 10 g batch with the composition 5·0 CuO: 1·0 V_2O_5:6·0 KVO_3 was placed in a Pt crucible, heated

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* On leave of absence from the Central Research Dept., E. I. du Pont de Nemours, Wilmington, Delaware, U.S.A.

to 1000°C for 4 h, cooled at 10°C/h to 500°C, and quenched in air. After dissolving the KVO_3 flux in water, dark-red crystals of both plate-like and needle-like habits were found. Powder diffraction patterns taken with a Hägg–Guinier camera (25°C, Cu $K\alpha$ radiation) indicated the same phase reported by Brisi & Molinari (1958). X-ray precession photographs showed the space group to be $P2_1/c$ with cell dimensions refined from the Guinier powder data: $a=8{\cdot}393(2)$, $b=6{\cdot}0652(8)$, $c=16{\cdot}156(3)$ Å, $\beta=108{\cdot}09$ (2)°, $V=781{\cdot}8$ Å^3. Other crystal data are: F.W. 579·6, $d_x=4{\cdot}92$ g cm^{-3}, $d_m=5{\cdot}0$ g cm^{-3} and $Z=4$.

A sphere ground to a radius of 0·15 mm ($\mu r=2{\cdot}44$) was used to obtain intensity data, which were collected on a Syntex automatic diffractometer using Mo $K\alpha$ radiation, 4° take-off angle, a graphite monochromator ($2\theta=12°$) and a scintillation detector. Reflexions were scanned in the 2θ–θ mode at variable rates from 4·0–24·0°/min depending on the peak count through an angle of 2° plus the α_1–α_2 separation. Background counts were made at the extreme of each scan for times equal to the peak count. The $\bar{4}02$ reflexion was chosen as an internal standard and monitored every 50 reflexions. No significant deviation in its intensity was

Table 1 *Observed and calculated structure factors for* $Cu_5V_2O_{10}$

K	L		|FOBS|	|FCLC|
K	L		H = 0	
0	2	•	0	1
0	4		142	137
0	6		19	18
0	8		44	42
0	10		318	314
0	12		122	119
0	14		132	131
0	16		119	117
0	18		35	35
1	1		21	19
1	2	•	4	0
1	3		46	42
1	4		180	178
1	5	•	10	7
1	6		88	93
1	7		90	89
1	8		150	149
1	9		41	41
1	10		258	258
1	11		20	20
1	12		48	49
1	13		52	52
1	14		51	50
1	15		38	38
1	16		128	129
1	17		74	75
1	18		75	77
1	19		17	19
2	0		216	221
2	1		111	111
2	2		106	114
2	3		181	188
2	4		209	211
2	5		25	25
2	6		279	294
2	7		181	191
2	8		91	90
2	9	•	10	9
2	10		35	15
2	11	•	5	0
2	12		17	17
2	13		34	33
2	14	•	5	7
2	15	•	5	4
2	16		37	35
2	17	•	4	2
2	18		27	25
2	19		47	49
3	1		14	13
3	2		18	18
3	3		45	44
3	4		149	149
3	5	•	9	1
3	6		60	58
3	7		80	78
3	8		35	34
3	9		168	170
3	10		122	121
3	11		80	90
3	12		16	15
3	13		34	30
3	14		73	73
3	15		29	28
3	16		130	134
3	17		64	65
3	18		16	15
4	0		214	221
4	1		276	287
4	2		83	91
4	3		137	135
4	4	•	7	0
4	5		31	29
4	6		58	58
4	7		50	49
4	8	•	12	11
4	9		155	157
4	10		96	96
4	11		92	93
4	12		78	78
4	13		138	139
4	14		59	58
4	15		23	23
4	16		18	16
4	17		84	86
5	1		35	35
5	2	•	5	5
5	3		56	56
5	4		68	69
5	5		50	48
5	6		26	27
5	7		73	73
5	8		51	51
5	9		136	140
5	10		74	74
5	11		34	33
5	12		69	66
5	13	•	10	9
5	14		33	36
5	15		16	12
6	0		59	58
6	1		53	54
6	2		99	98
6	3		99	99
6	4	•	8	3
6	5		38	37
6	6		16	13
6	7		136	139
6	8		54	53
6	9	•	13	10
6	10		37	38
6	11	•	13	8
6	12		39	39
7	1		17	13
7	2	•	10	9
7	3		54	53
7	4		37	37
7	5		33	32
7	6	•	7	1
7	7		22	22
7	8		60	62
7	9		52	53
K	L		H = 1	
0	0		116	114
0	-2		39	39
0	4		167	153
0	-4		55	53
0	6		22	22
0	-6		273	261
0	8		162	155
0	-8		38	37
0	10		185	196
0	-10		85	82
0	12		28	26
0	-12	•	11	13
0	14		26	24
0	-14		38	39
0	-16		183	188
0	16		19	16
0	18		58	58
0	-18		19	13
0	-20		74	73
1	0		146	144
1	1		29	28
1	-1		29	26
1	2		23	21
1	-2		15	13
1	3		21	21
1	-3		27	26
1	4		258	250
1	-4		45	44
1	5		53	52
1	-5		57	52
1	6	•	14	11
1	-6		207	200
1	7		49	48
1	-7		36	35
1	8		15	13
1	9	•	14	12
1	-9		24	23
1	10		66	66
1	-10		93	92
1	11		48	46
1	-11		52	53
1	12		20	16
1	-12		51	50
1	13	•	9	9
1	-13		68	68
1	14		99	98
1	-14	•	12	11
1	15		19	20
1	-15		21	19
1	-16	•	6	1
1	16	•	17	17
1	17		35	36
1	-17		24	23
1	18		53	53
1	19		27	27
1	-19		34	34
1	-20	•	15	11
2	0		205	209
2	1		112	112
2	-1	•	7	3
2	2		24	23
2	-2		119	121
2	3		94	92
2	-3		183	186
2	4		185	187
2	-4		131	129
2	5	•	12	17
2	-5		84	80
2	6		165	167
2	-6	•	13	5
2	7		140	140
2	-7		24	25
2	8	•	9	7
2	-8	•	4	1
2	9		48	45
2	-9		99	98
2	10		84	85
2	-10		208	205
2	11		43	43
2	12		39	39
2	-12		133	131
2	13		95	94
2	-13		88	87
2	14		175	175
2	-14		37	37
2	15		37	36
2	-15		13	18
2	-16		49	50
2	16		99	99
2	17		48	48
2	-17	•	15	14
2	18	•	1	2
2	-18		25	22
2	-19		65	66
3	0		140	135
3	1		37	32
3	-1		42	43
3	2		51	53
3	-2		26	24
3	3		67	65
3	-3		17	17
3	4		127	130
3	-4	•	12	13
3	5		135	134
3	-5		50	49
3	6		30	31
3	-6		158	159
3	7	•	5	4
3	-7		31	29
3	8	•	7	7
3	-8		52	52
3	9	•	12	8
3	-9		44	42
3	10		99	100
3	-10	•	17	14
3	11	•	15	13
3	-11		92	94
3	12		22	21
3	-12		75	74
3	13		65	65
3	-13		36	35
3	-14		20	19
3	14	•	12	9
3	-15		20	20
3	15		57	57
3	-16		47	49
3	17		31	29
3	-18		25	27
4	0		25	25
4	1		82	83
4	-1		56	57
4	2		17	12
4	-2		52	51
4	3		103	105
4	-3		30	29
4	4		22	21
4	-4		71	70
4	5		87	87
4	-5		158	158
4	6		23	23
4	-6		66	64
4	7		91	86
4	-7		75	75
4	8		71	71
4	-8		36	36
4	9		17	17
4	-9		36	35
4	10		67	65
4	-10		83	83
4	11		93	92
4	-11	•	13	9
4	12		17	16
4	-12		21	20
4	-13	•	10	8
4	13		25	25
4	14		35	35
4	-14		19	19
4	15	•	8	11
4	-15		94	95
4	16		25	24
4	-16		70	71
4	-17		41	43
5	0		68	66
5	1	•	8	2
5	-1	•	13	11
5	2		54	53
5	-2		49	48
5	3		64	65
5	-3		46	46
5	4		70	69
5	-4		19	17
5	5		94	95
5	-5		41	40
5	6		94	95
5	-6		61	61
5	7		28	27
5	-7		53	52
5	8		26	25
5	-8		24	24
5	9	•	5	4
5	-9	•	8	0
5	10	•	6	4
5	-10	•	18	17
5	-11		54	53
5	11	•	15	12
5	12		35	35
5	-12		78	75
5	13		47	47
5	-13		37	36
5	14	•	15	17
5	-14		48	49
5	-15		25	6
6	0		18	16
6	1		97	100
6	-1		46	44
6	2		24	22
6	-2		67	67
6	3		111	110
6	-3		115	117
6	4		26	26
6	-4		98	99
6	5		27	8
6	-5		29	29
6	6		38	36
6	-6		25	22
6	7		106	106
6	-7		70	70
6	8		54	57
6	-8		32	31
6	9		75	74
6	-9		90	90
6	10		51	50
6	-10		52	51
6	11		47	47
6	-11	•	19	19
6	12	•	7	12
6	-13		77	77
7	0		42	41
7	1	•	4	1
7	-1		29	30
7	2		24	27
7	-2		39	38
7	-3	•	13	11
7	4	•	10	8
7	-4		21	22
7	5		46	47
7	-5		48	48
7	6		77	77
7	-6		53	53
7	7	•	15	15
7	-7	•	15	15
7	8	•	8	7
7	-8		20	17
7	-9		38	39
K	L		H = 2	
0	2		141	143
0	-2		41	39
0	4		223	227
0	-4	•	1	0
0	6		140	141
0	-6		257	258
0	8	•	3	7
0	-8	•	15	17
0	10		47	48
0	-10		190	191
0	12		33	32
0	-12	•	10	8
0	14		90	88
0	-14		23	22
0	-16		59	60
0	16		79	78
0	18		21	17
0	-18		54	55
0	-20		59	61
1	1		64	65
1	-1	•	5	2
1	2		57	55
1	-2		98	98
1	3	•	5	6
1	-3		29	28
1	4		35	35
1	-4		36	35
1	5	•	10	11
1	-5		34	34
1	6		55	56
1	-6		169	177
1	7		49	50
1	-7		19	20
1	8		40	43
1	-8		48	48
1	9		30	31
1	-9	•	14	17
1	10		110	110
1	-10		38	36
1	11		82	81
1	12		65	65
1	-12		63	62
1	13	•	3	9
1	-13		46	47
1	14		71	68
1	-14		74	75
1	-15		36	38
1	15	•	9	12
1	-16		177	182
1	16	•	13	12
1	-17	•	12	10
1	17		33	33
1	18	•	17	16
1	-18	•	19	19
1	-19	•	16	15
1	-20		34	33
2	0		137	143
2	1		120	122
2	-1	•	8	4
2	2		109	110
2	-2		166	171
2	3		38	39
2	-3		57	68
2	4		48	47
2	-4		22	22
2	5	•	13	10
2	-5	•	12	10
2	6		24	23
2	-6		63	63
2	7		45	45
2	-7		70	69
2	8		85	84
2	-8		94	95
2	9	•	3	1
2	-9		95	93
2	10		119	118
2	-10	•	13	10
2	-11		51	49
2	11		42	41
2	-12		162	163
2	12		23	20
2	13		28	27
2	-13		46	47
2	14		38	37
2	-14		28	25
2	-15		61	60
2	15	•	17	17
2	-16		82	82
2	16	•	8	8
2	17		43	46
2	-18		31	35
2	-19		36	39
2	-20	•	10	10
3	0	•	10	9
3	1		52	52
3	-1	•	8	5
3	2	•	13	10
3	-2		77	77
3	3		42	41
3	-3		42	41
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3	-4		41	43
3	5		34	32
3	-5		52	51
3	6		61	62
3	-6		117	115
3	7	•	12	10
3	-7		82	80
3	8		93	94
3	-8		19	18
3	9		50	50
3	-9	•	16	15
3	-10		62	62
3	10		95	97
3	-11		23	22
3	11		78	78
3	12		23	22
3	-12		61	57
3	13		48	47
3	-13		38	36
3	-14		34	32
3	14	•	10	5
3	-15		104	102
3	15	•	7	7
3	16	•	12	9
3	-16		90	88
3	-17		70	68
3	-18		22	23
3	-19		24	26
4	0	•	8	5
4	1		17	14
4	-1		19	17
4	2	•	8	4
4	-2		58	59
4	3		156	158
4	-3		54	53
4	4		106	107
4	-4		35	34
4	5		35	31
4	-5		119	119
4	6		75	75
4	-6		94	95
4	7		100	98
4	-7		133	136
4	8	•	10	10
4	-8		34	34
4	9		40	41
4	-9		61	60
4	10		23	22
4	-10		56	57
4	11		38	38
4	-11		25	23
4	-12		31	32
4	12	•	18	18
4	-13		45	46
4	13		61	60
4	14		33	35
4	-14	•	6	6
4	15	•	5	4
4	-15		36	33
4	-17		20	19
5	0		59	59
5	1		38	38
5	-1		35	34
5	2		32	31
5	-2		24	23
5	3		32	32
5	-3		58	58
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5	-5		60	61
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5	-7		66	64
5	8		43	44
5	-8		20	18
5	9		30	28
5	-9	•	8	6
5	10		31	29
5	-10		28	28
5	11		74	70
5	12		34	32
5	-12	•	10	6
5	13		29	32
5	-13		22	22
5	-14		35	37
5	-15		99	100
5	-16		54	55
6	0	•	5	2
6	1		117	117
6	-1		23	20
6	2		52	53
6	-2		41	38
6	3		21	19
6	-3		85	82
6	4		51	51
6	-4		39	38
6	5		37	34
6	-5		19	19
6	6		36	38
6	-6		27	22
6	7		31	33
6	-7		38	39
6	8	•	16	15
6	-8		59	59
6	9	•	10	5
6	-9		64	54
6	10		30	29
6	-10		27	26
6	11		61	64
6	-11		75	75
6	-12	•	7	6
6	-13		66	65
7	0		33	30
7	1	•	17	16
7	-1	•	17	16
7	2		20	29
7	-2	•	4	4
7	3	•	16	16
7	-3		59	60
7	4		22	23
7	-4	•	12	13
7	-5		23	21
7	-6	•	17	12
7	7		65	57
7	-7		40	41
7	-8		33	36
7	-9	•	19	19
K	L		H = 3	
0	0		37	38
0	2		149	152
0	-2		319	314
0	4		117	118
0	-4	•	2	1
0	6	•	6	1
0	-6		124	119
0	8		35	34
0	-8		87	88
0	10		69	66
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Table 1 (*cont.*)

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3	8		163	152
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2	-14	*	3	6
2	-16		49	50
2	-17		69	68
2	-18		56	56
3	5		64	64
3	6		29	30
3	7		32	34
3	8		22	22
3	9		30	31
3	-12		29	29
3	-13	*	7	7
3	-14		46	46
3	-15		63	61
3	-16		27	28
3	-17	*	18	16
4	0	*	10	8
4	1	*	13	14
4	-1		65	65
4	2		25	27
4	3	*	4	3
4	4		21	21
4	5		31	30
4	6	*	14	9
4	7		30	29
4	-7	*	8	2
4	-8		25	26
4	-9	*	3	5
4	-10		34	33
4	-11		31	31
4	-12	*	15	15
4	-13		77	78
4	-14		67	68
4	-15		91	91
5	0		31	33
5	0		31	33
5	1		49	49
5	-1		50	52
5	2	*	13	11
5	-2	*	10	2
5	3		76	76
5	-3		35	35
5	4		34	34
5	-4		42	43
5	-5	*	11	10
5	-6		46	45
5	-7		19	18
5	-8	*	16	17
5	-9	*	5	4
5	-10		19	19
5	-11		44	46
5	-12		32	33
6	-3		43	39
6	-4		31	30
6	-5	*	4	2
6	-6		32	34
K	L		H = 8	
0	4		57	57
0	6		235	233
0	8		36	34
0	-14		81	80
0	-16		21	21
0	-18		56	55
1	3		49	40
1	5		28	27
1	6		25	28
1	7		41	40
1	8		61	62
1	-13	*	12	8
1	-14		54	53
1	-15		19	20
1	-16		46	46
1	-17	*	13	15
1	-18		55	55
2	2		62	61
2	3		45	45
2	4	*	3	1
2	5		29	27
2	6		87	87
2	7		37	36
2	-11	*	10	9
2	-12	*	12	12
2	-13		40	39
2	-14		83	80
2	-16		55	53
2	-17		56	54
3	0		27	26
3	1		36	33
3	-1		100	102
3	2		23	23
3	-2		22	24
3	3		21	20
3	-3		62	63
3	4	*	2	2
3	5	*	11	11
3	6		53	54
3	-7	*	4	5
3	-8		26	25
3	-9	*	10	4
3	-10		74	72
3	-11		55	53
3	-12	*	4	5
3	-13		23	23
3	-14		44	41
3	-16		40	39
4	0		30	29
4	1		19	18
4	-1		72	72
4	2	*	10	9
4	-2	*	11	9
4	3		82	82
4	-3		79	77
4	4		51	51
4	-4		56	55
4	-5		65	65
4	-6		72	72
4	-7		93	91
4	-8		45	46
4	-9		76	77
4	-10		34	32
4	-11		121	121
4	-12	*	9	7
4	-13		62	61
5	0	*	17	19
5	-1		75	74
5	-2	*	10	11
5	-3		74	74
5	-4	*	17	16
5	-5	*	17	15
5	-6		28	28
5	-7		26	22
5	-8		56	56
5	-9	*	9	9
K	L		H = 9	
0	0		137	135
0	2		35	33
0	-2	*	16	17
0	4		39	36
0	-8	*	7	6
0	-10		231	229
0	-12		34	32
0	-14		46	45
0	-16		25	25
1	0		159	150
1	1	*	15	15
1	-1	*	15	18
1	2		24	23
1	-2		21	21
1	3		32	32
1	-3		46	47
1	4		27	25
1	-4		36	34
1	5		52	51
1	-5		49	49
1	-6	*	10	11
1	-7		32	33
1	-8		25	28
1	-10		20	9
1	-11		30	29
1	-12		43	42
1	-13	*	8	9
1	-14		79	80
1	-15	*	14	15
1	-16		66	64
2	0	*	10	9
2	-1	*	15	19
2	2	*	18	19
2	-2	*	12	14
2	3		51	50
2	-3		95	96
2	4		33	34
2	-4		194	198
2	-5		47	47
2	-6		87	87
2	-7		59	59
2	-8		58	57
2	-9		37	35
2	-10		69	68
2	-11		30	29
2	-12		28	30
2	-13		87	90
2	-14		124	122
2	-15		23	22
3	0		55	57
3	1		48	44
3	-1		75	77
3	2		24	25
3	-2		27	27
3	-3		21	20
3	-4		56	54
3	-5		41	42
3	-6		25	26
3	-7	*	14	13
3	-8		64	65
3	-9		20	19
3	-10		21	19
3	-12		43	42
3	-13		50	50
4	-1		50	50
4	-2	*	15	16
4	-3		23	20
4	-4		59	61
4	-5		39	39
4	-6		34	33
4	-7		33	30
4	-8		20	20
4	-9		94	95
4	-10		78	76
K	L		H = 10	
0	0		92	94
0	-2		27	27
0	-4		93	92
0	-6		45	44
0	-8		81	90
0	-10	*	11	11
0	-12	*	10	6
1	0		108	138
1	1		52	53
1	-1		39	39
1	-2	*	11	11
1	-3		45	47
1	-4	*	5	2
1	-5		17	15
1	-6		97	98
1	-7	*	1	5
1	-8		49	45
1	-9		48	47
1	-10		92	89
1	-11	*	11	5
1	-12		58	59
1	-13		27	26
2	0	*	14	1
2	-1	*	11	1
2	-2	*	8	9
2	-3	*	15	23
2	-5	*	11	7
2	-6		47	49
2	-7	*	8	5
2	-8		47	45
2	-9		62	53
2	-10		85	85
2	-11	*	6	1
2	-12		50	47
3	-4	*	11	13
3	-5		50	50
3	-6		32	30
3	-7		59	50

* Indicates unobserved reflexions.

noted. A total of 1629 reflexions were measured within a 2θ value of 82°; 1254 were considered to be observed. A reflexion was considered to be unobserved if the intensity was less than three times the standard deviation. The intensities were corrected for Lorentz and polarization factors and for absorption using the X-ray 67 Program System for X-ray Crystallography written by J. M. Stewart, University of Maryland and adapted to the CDC computer by H. D. Grundy.

The positions of the metal atoms were obtained from *h0l* and *0kl* Patterson projections. Electron-density difference maps were used to locate the 10 oxygen atoms. All atoms were placed in equipoint 4(*e*) of the space group. Several cycles of refinement using the full-matrix least-squares program *CUDLS*, written by J. S. Stephens of this laboratory reduced

$$wR=\left\{\frac{\sum w||F_o|-|F_c||^2}{\sum w|F_o|^2}\right\}^{1/2}$$

to 0·056 with isotropic temperature factors, and the secondary extinction coefficients calculated according to Zachariasen (1963). A Cruickshank weighting scheme was used in which $w=(5\cdot44-0\cdot0322|F_o|+0\cdot00031|F_o|^2)_{-}{}^{1}$. The weights w were chosen so as to make $w||F_o|-|F_c||^2$ independent of the variation in F_o. Further refinement using anisotropic temperature factors reduced R to 0·026 and wR to 0·032 for all reflexions. In the final refinement unobserved reflections were given zero weight if $F_{\rm calc}<F_{\rm min}$ and were given the value of $0\cdot9F_{\rm min}$ if $F_{\rm calc}>F_{\rm min}$. The secondary extinction parameter refined according to the method of Larson (1967) was found to be $c=7\cdot00\times10^{-7}$. The standard deviation, S, of a reflexion of unit weight was 0·98. Scattering factors Cu^0, V^0, and O^0 were taken from Cromer & Waber (1965) with real and imaginary anomalous-dispersion terms given by Cromer (1965). Table 1 lists the observed and calculated structure factors and Table 2 lists the atomic coordinates with anisotropic temperature factors.

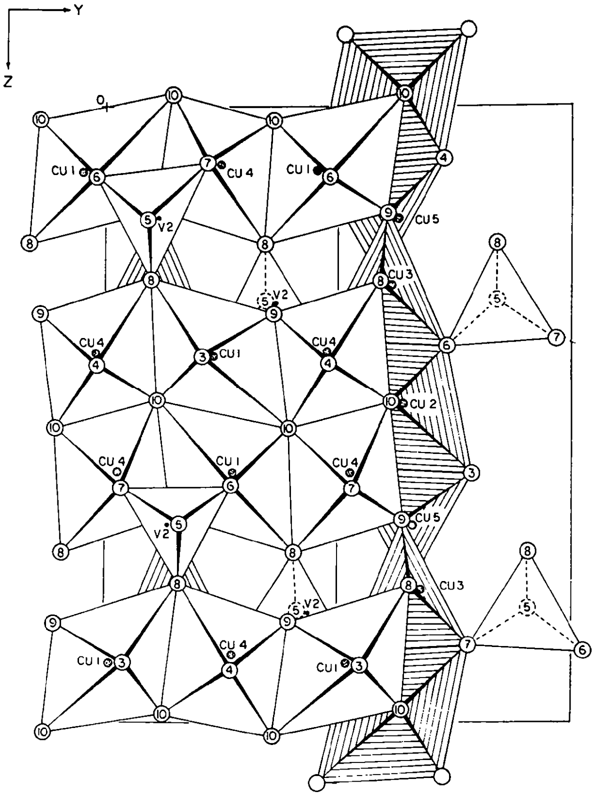

Fig. 1. A partial *yz* projection of two unit cells of $Cu_5V_2O_{10}$ arrangement. The shaded polyhedra belong to the zigzag chain containing the two trigonal bipyramids.

Results and discussion

The structure of $Cu_5V_2O_{10}$ can be described in terms of a polyhedral model. Cu(1), Cu(2) and Cu(4) are octahedrally coordinated, Cu(3) and Cu(5) each have five oxygen-atom neighbours in the form of trigonal bipyramids, and the V atoms are tetrahedrally coordinated. Cu(1) and Cu(4) form continous double chains with the configuration:

$$\begin{array}{ccccc} \mathrm{Cu(1)} & - & \mathrm{Cu(4)} & - & \mathrm{Cu(1)} \\ | & & | & & | \\ \mathrm{Cu(1)} & - & \mathrm{Cu(4)} & - & \mathrm{Cu(1)} \end{array}$$

shown in Fig. 1. These chains run along the y axis at $x \simeq 0$ and 1 and are linked to each other by V(2) atoms. Cu(2), Cu(3), and Cu(5) polyhedra form zigzag chains running along the z axis as shown in Fig. 2. The Cu(2) octahedron shares one edge with two equatorial oxygen atoms [O(6) and O(7) of Cu(3)], and the other edge with two equatorial oxygen atoms [O(3) and O(4) of Cu(5)]. Cu(3) shares one apical, O(1), and one equatorial oxygen atom, O(9), with Cu(5) to form the jog in the Cu(3)–Cu(2)–Cu(5) chain.

The chains along y are connected to the chains along z by extensive edge sharing between Cu(2) and Cu(4) octahedra and Cu(2) and Cu(1) octahedra, between the Cu(5) trigonal bipyramid and Cu(1) and Cu(4), and between the Cu(3) trigonal bipyramid with Cu(1) and Cu(4). There are two networks formed by linking the y chains with the z chains. These are located at $x \simeq \frac{1}{4}$ and $\frac{3}{4}$ and are linked together by the V(1) tetrahedra. The bond lengths and bond angles are given in Table 3.

The shortest Cu–Cu distance (2·869 Å) is across the

Table 2. *Final atom parameters for* $Cu_5V_2O_{10}$

Standard deviations are given in parentheses.

Anisotropic thermal parameters are calculated from $\beta_{ij} = 2\pi^2 b_i b_j U_{ij}$ where $T = \exp[-(\beta_{11}h^2 + 2\beta_{12}hk + \ldots)]$ is the temperature factor appearing in the structure factor equation and b_i's are the reciprocal-lattice vectors. All values of the thermal parameters are multiplied by 10^4.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu(1)	0·06052 (9)	−0·05305 (12)	0·10166 (5)	68 (4)	85 (4)	96 (4)	−10 (3)	26 (3)	−36 (3)
Cu(2)	0·26391 (9)	0·24380 (12)	0·48448 (5)	66 (4)	101 (4)	72 (3)	8 (3)	19 (3)	29 (3)
Cu(3)	0·16051 (10)	0·18317 (14)	0·28887 (14)	65 (4)	223 (4)	62 (4)	−2 (3)	15 (3)	30 (3)
Cu(4)	0·04069 (10)	0·45348 (12)	0·09186 (12)	116 (4)	85 (4)	87 (4)	33 (3)	46 (3)	28 (3)
Cu(5)	0·37081 (10)	0·22379 (14)	0·17954 (5)	48 (4)	219 (4)	79 (4)	14 (3)	19 (3)	34 (3)
V(1)	0·43036 (13)	0·71053 (16)	0·09887 (6)	50 (5)	60 (5)	56 (4)	0 (4)	13 (4)	−14 (4)
V(2)	0·21585 (13)	0·69313 (16)	0·32889 (6)	52 (5)	65 (5)	70 (5)	1 (4)	21 (4)	10 (4)
O(1)	0·4026 (6)	0·1961 (8)	0·3048 (3)	104 (22)	164 (21)	54 (18)	−15 (17)	0 (16)	2 (16)
O(2)	0·4910 (6)	0·2546 (8)	0·4820 (3)	67 (21)	180 (22)	86 (20)	−5 (17)	9 (16)	−4 (16)
O(3)	0·2930 (6)	0·9213 (8)	0·0983 (6)	67 (21)	173 (22)	221 (22)	20 (18)	43 (17)	−62 (18)
O(4)	0·3208 (6)	0·4582 (8)	0·0849 (3)	141 (23)	135 (20)	70 (18)	−22 (18)	18 (16)	−13 (16)
O(5)	0·4033 (6)	0·6853 (8)	0·3161 (3)	111 (24)	203 (23)	156 (20)	−8 (19)	70 (17)	3 (18)
O(6)	0·1752 (6)	0·4610 (7)	0·3867 (3)	86 (20)	82 (20)	100 (18)	27 (16)	40 (16)	13 (15)
O(7)	0·1878 (6)	0·9371 (7)	0·3778 (3)	151 (22)	94 (20)	106 (18)	−18 (17)	55 (16)	11 (16)
O(8)	0·0760 (6)	0·6854 (8)	0·2236 (3)	83 (21)	241 (23)	86 (18)	18 (18)	27 (16)	20 (17)
O(9)	0·1345 (6)	0·2131 (7)	0·1668 (3)	101 (22)	91 (19)	70 (17)	−14 (16)	30 (15)	20 (15)
O(10)	0·0315 (6)	0·2116 (7)	0·4764 (3)	86 (22)	116 (20)	74 (17)	10 (16)	32 (15)	8 (15)

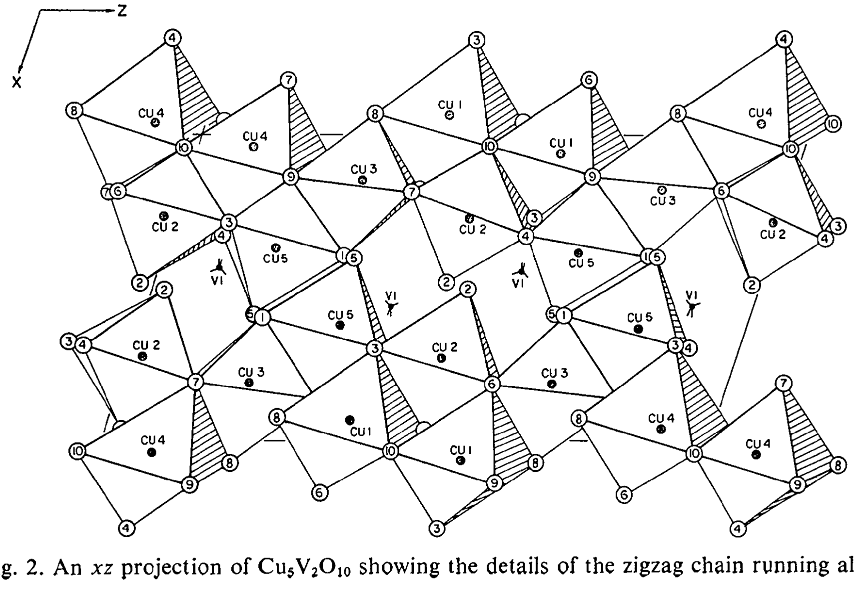

Fig. 2. An xz projection of $Cu_5V_2O_{10}$ showing the details of the zigzag chain running along z.

non-equatorial shared edge, [O(1)–O(9)], of the two trigonal bipyramids. The two other Cu–Cu distances less than 3 Å are across the O(10)–O(10*b*) shared edge, with the Cu(4)–Cu(4*b*) distance equal to 2·887 Å and across the O(6)–O(10) shared edge, with the Cu(1)–Cu(2) distance equal to 2·917 Å. Only the first and last of these differ significantly (Åsbrink & Norrby, 1970) and are considerably longer than the Cu–Cu distances of 2·51 Å in $Cu_{4-x}Mo_3O_{12}$ (Katz, Kasenally, & Kihlborg, 1971).

The distances in the octahedra containing Cu(1) and Cu(2) are typical of those of Cu^{2+}, in which there are four short distances of about 1·95 Å and 2 longer distances of 2·30–2·80 Å (Shannon & Calvo, 1972; Abrahams, Bernstein & Jamieson, 1968) presumably indicative of Jahn–Teller distortion. Cu(4) is also octahedrally coordinated but it is interesting to note that the two elongated bonds in the Cu(4) octahedron are not the axial bonds but the adjacent bonds to O(4) and O(8). In other Jahn–Teller distorted CuO_6 octahedra, one generally finds the long Cu–O bonds on opposite sides of the octahedra, *e.g.* $CuMoO_4$ (Abrahams, Bernstein & Jamieson, 1968); $Cu_3V_2O_8$ (Shannon & Calvo, 1972*a*); $CuWO_4$ (Kihlborg & Gebert, 1970); $Cu_{4-x}Mo_3O_{12}$ (Katz, Kasenally & Kihlborg, 1971); $Cu_3As_2O_8$ (Poulsen & Calvo, 1968); Cu_2OSO_4 (Flügel-Kahler, 1963); and CuO (Åsbrink & Norrby, 1970).

The mean Cu–O distances in the octahedra are signi-

Table 3. *Bond lengths and angles in* $Cu_5V_2O_{10}$*

V(1)—O(1)	1·744 (4) Å	O(4)—V(1)—O(3)	108·8 (3)°	O(3)—V(1)—O(1*a*)	113·1 (3)°
V(1)—O(2)	1·658 (5)	O(4)—V(1)—O(1*a*)	108·3 (2)	O(3)—V(1)—O(2*a*)	108·0 (3)
V(1)—O(3)	1·721 (5)	O(4)—V(1)—O(2*a*)	111·0 (3)	O(1*a*)—V(1)—O(2*a*)	107·8 (3)
V(1)—O(4)	1·764 (4)				
⟨V(1)—O⟩	1·722				
V(2)—O(5)	1·650 (5)	O(6)—V(2)—O(5)	112·9 (3)	O(5)—V(2)—O(7)	110·7 (3)
V(2)—O(6)	1·780 (4)				
V(2)—O(7)	1·728 (4)	O(6)—V(2)—O(7)	111·2 (3)	O(5)—V(2)—O(8)	104·8 (3)
V(2)—O(8)	1·742 (4)	O(6)—V(2)—O(8)	108·1 (2)	O(7)—V(2)—O(8)	108·9 (3)
⟨V(2)—O⟩	1·725				
Cu(1)–O(3)	1·973 (5)	O(3)—Cu(1)–O(6*a*)	175·8 (2)	O(6*a*)—Cu(1)–O(10*a*)	83·5 (2)
Cu(1)–O(9)	1·922 (4)	O(3)—Cu(1)–O(8)	88·2 (2)	O(6*a*)—Cu(1)–O(10*c*)	99·4 (2)
Cu(1)–O(10*a*)	1·903 (4)	O(3)—Cu(1)–O(9)	85·8 (2)	O(8)—Cu(1)–O(9)	100·0 (2)
Cu(1)–O(6)	2·046 (5)	O(3)—Cu(1)–O(10*a*)	97.2 (2)	O(8)—Cu(1)–O(10*a*)	87·6 (2)
Cu(1)–O(8)	2·501 (5)	O(3)—Cu(1)–O(10)*c*)	84·6 (2)	O(8)—Cu(1)–O(10*c*)	172·5 (2)
Cu(1)–O(10*c*)	2·852 (4)	O(6*a*)–Cu(1)–O(8)	76·7 (2)	O(9)—Cu(1)–O(10*c*)	73·8 (2)
⟨Cu(1)–O⟩	2·200	O(6*a*)–Cu(1)–O(9)	94·1 (2)	O(10*a*)-Cu(1)–O(10*c*)	98·5 (2)
Cu(2)–O(2)	1·920 (5)	O(2)—Cu(2)–O(6)	95·1 (2)	O(6)—Cu(2)–O(4*c*)	171·5 (2)
Cu(2)–O(10)	1·924 (5)	O(2)—Cu(2)–O(7)	93·1 (2)	O(6)—Cu(2)–O(3*c*)	88·7 (2)
Cu(2)–O(4)	1·970 (4)	O(4)—Cu(2)–O(10)	173·8 (2)	O(7)—Cu(2)–O(10)	80·8 (2)
Cu(2)–O(6)	2·014 (4)	O(2)—Cu(2)–O(4*c*)	92·9 (2)	O(7)—Cu(2)–O(4*c*)	92·9 (2)
Cu(2)–O(7)	2·481 (4)	O(2)—Cu(2)–O(3*c*)	96·2 (2)	O(7)—Cu(2)–O(3*c*)	170·6 (2)
Cu(2)–O(3)	2·702 (5)	O(6)—Cu(2)–O(7)	89·6 (2)	O(10)—Cu(2)–O(4*c*)	88·5 (2)
⟨Cu(2)–O⟩	2·168	O(6)—Cu(2)–O(10)	83·9 (2)	O(10)—Cu(2)–O(3*c*)	89·9 (2)
				O(4*c*)—Cu(2)–O(3*c*)	87·6 (2)
Cu(3)–O(8*a*)	1·932 (5)	O(1)—Cu(3)–O(6)	92·8 (2)	O(6)—Cu(3)–O(9)	127·1 (2)
Cu(3)–O(9)	1·924 (4)	O(1)—Cu(3)–O(7)	93·0 (2)	O(7)—Cu(3)–O(8*a*)	88·0 (2)
Cu(3)–O(1)	1·969 (5)	O(1)—Cu(3)–O(8*a*)	177·0 (2)	O(7)—Cu(3)–O(9)	138·2 (2)
Cu(3)–O(7)	2·034 (4)	O(1)—Cu(3)–O(9)	85·1 (2)	O(8*a*)—Cu(3)–O(9)	96·1 (2)
Cu(3)–O(6)	2·287 (4)	O(6)—Cu(3)–O(7)	94·7 (2)		
⟨Cu(3)–O⟩	2·029	O(6)—Cu(3)–O(8*a*)	84·3 (2)		
Cu(4)–O(9)	1·902 (4)	O(4)—Cu(4)–O(7*a*)	169·7 (2)	O(7*a*)—Cu(4)–O(8)	72·9 (2)
Cu(4)–O(10*a*)	1·903 (4)	O(4)—Cu(4)–O(9)	79·6 (2)	O(7*a*)—Cu(4)–O(10*a*)	91·4 (2)
Cu(4)–O(10*c*)	2·097 (4)	O(4)—Cu(4)–O(10*c*)	74·2 (2)	O(9)—Cu(4)–O(10*c*)	95·4 (2)
Cu(4)–O(7)	2·124 (5)	O(4)—Cu(4)–O(8)	100·1 (2)	O(9)—Cu(4)–O(8)	88·5 (2)
Cu(4)–O(4)	2·388 (5)	O(4)—Cu(4)–O(10*a*)	96·0 (2)	O(9)—Cu(4)–O(10*a*)	173·7 (2)
Cu(4)–O(8)	2·490 (4)	O(7*a*)–Cu(4)–O(9)	92·4 (2)	O(10*c*)–Cu(4)–O(8)	172·4 (2)
⟨Cu(4)–O⟩	2·151	O(7*a*)–Cu(4)–O(10*c*)	113·4 (2)	O(10*c*)–Cu(4)–O(10*a*)	87·7 (2)
				O(8)—Cu(4)–O(10*a*)	87·9 (2)
Cu(5)–O(5)	1·890 (5)	O(1)—Cu(5)–O(3)	117·1 (2)	O(3)—Cu(5)–O(9)	78·8 (2)
Cu(5)–O(9)	1·930 (5)	O(1)—Cu(5)–O(4)	139·9 (2)	O(3)—Cu(5)–O(5*a*)	91·6 (2)
Cu(5)–O(1)	1·964 (4)	O(1)—Cu(5)–O(9)	85·0 (2)	O(4)—Cu(5)–O(9)	88·7 (2)
Cu(5)–O(4)	2·034 (5)	O(1)—Cu(5)–O(5*a*)	97·9 (2)	O(4)—Cu(5)–O(5*a*)	94·9 (2)
Cu(5)–O(3)	2·230 (5)	O(3)—Cu(5)–O(4)	100·3 (2)	O(9)—Cu(5)–O(5*a*)	170·2 (2)
⟨Cu(5)–O⟩	2·010				

* Symmetry transformations: $a=-x,\ \frac{1}{2}+y,\ \frac{1}{2}-z$; $b=-x,\ -y,\ -z$; $c=x,\ \frac{1}{2}-y,\ \frac{1}{2}+z$

Table 4. *Comparison of mean octahedral* Cu–O *distances with distortion*

Compound	$\bar{R}$, (Å)*	Distortion, $\Delta=\langle(\Delta R/R)^2\rangle$	Reference†
$Cu(NH_4)_2(SO_4)_2.6H_2O$	2·098 (1)	0·0027	69 ACBCA 25 676
$CuVO_3$	2·130 (2)	0·0035	72 JSSCB 5 446
$CuSO_4.5H_2O$	2·116 (10)	00·078	62 PRLAA 266 95
$CuWO_4$	2·115 (4)	0·0090	70 ACBCA 26 1020
$Cu_3SO_4(OH)_4$	2·112 (20)	0·0093	63 NATUA 197 70
$Na_2Cu(SO_4)_2\ 2H_2O$	2·117 (29)	0·0097	61 ACCRA 14 738
$Cu_2AsO_4OH\ 3H_2O$	2·129 (12)	0·0099	66 ACCRA 21 437
$Cu_3AsO_4(OH)_3$	2·118 (12)	0·0103	65 ACCRA 18 777
$CuSO_4.3H_2O$	2·115 (5)	0·0107	68 ACBCA 24 508
$Cu_5V_2O_{10}$	2·151 (5)	0·0110	This paper
$CuSO_4.5H_2O$	2·120 (10)	0·0112	62 PRLAA 266 95
$Cu_3SO_4(OH)_4$	2·127 (20)	0·0119	63 NATUA 197 70
$Cu_3Mo_2O_9$	2·142 (26)	0·0121	71 ACBCA 27 2066
$CuMoO_4$	2·105 (9)	0·0140	68 JCPSA 48 2619
$Cu_3V_2O_8$	2·129 (4)	0·0147	72 CJCHA 50 3944
Cu_2OSO_4	2·153 (20)	0·0159	63 ACCRA 16 1009
$\beta\ Cu_2P_2O_7$	2·172 (15)	0·0175	68 CJCHA 46 605
$Cu_3As_2O_8$	2·169 (20)	0·0197	68 CJCHA 46 917
$Cu_5V_2O_{10}$	2·168 (10)	0·0199	This paper
$Cu_3V_2O_8$	2·162 (4)	0·0202	72 CJCHA 50 3944
$Cu_2AsO_4OH\ 3H_2O$	2·182 (12)	0·0208	66 ACCRA 21 437
$Cu_3AsO_4(OH)_3$	2·168 (12)	0·0233	65 ACCRA 18 777
$Cu_5V_2O_{10}$	2·200 (10)	0·0255	This paper
$\alpha\ Cu_2P_2O_7$	2·178 (5)	0·0289	67 ACCRA 22 665
CuO	2·232 (5)	0·0306	70 ACBCA 26 8

$\bar{R}=2\cdot093+3\cdot60\ \Delta$ Correlation coefficient $=0\cdot89$
Goodness of fit $=0\cdot016$

* $\bar{R}=$ mean octahedral Cu–O distance with average e.s.d. quoted by authors in parentheses.
† *Codens for Periodical Titles* (1966).

ficantly different: $\bar{R}$[Cu(1)–O] = 2·200 Å; $\bar{R}$[Cu(2)–O] = 2·168 Å; and $\bar{R}$[Cu(4)–O] = 2·151 Å. These differences have been shown to be a function of the distortion of the octahedron* and is a consequence of the non-linear shape of the bond strength–bond length curve which has been derived by Brown & Shannon (1973):

$$s_{Cu^{2+}}=0\cdot333\left(\frac{2\cdot084}{R}\right)^{5\cdot3} \qquad (1)$$

where s = the bond strength and R = bond length. Table 4 and Fig. 3 show the relationship between mean distance and degree of distortion. The correlation coefficient is 0·89 and indicates that most of the difference in mean Cu^{2+}–O distances can be explained by distortion.

The polyhedra about Cu(3) and Cu(5) are trigonal bipyramids. As in $Cu_3As_2O_8$ (Poulsen & Calvo, 1969), Cu_2OSO_4 (Flügel-Kahler, 1963) and Cu_3WO_6 (Gebert & Kihlborg, 1969) the apical bonds are the short bonds compared with the equatorial bonds (see Table 5). Both the Cu(3) and the Cu(5) trigonal bipyramids show angular distortion. The angles between equatorial oxygen atoms in Cu(3) range from 94–138° and those in Cu(5) range from 100° to 140°.

Table 5. *Comparison of apical and equatorial bonds in* $Cu–O_5$ *trigonal bipyramids*

Compound	Apical bonds (Å)	Equatorial bonds (Å)
Cu_2OSO_4	1·87, 1·91	2·01, 2·14, 2·14
Cu_3WO_6	1·921, 1·953	2·002, 2·060, 2·243
$Cu_3As_2O_8$	1·931, 1·933	1·993, 2·010, 2·157
	1·956, 1·976	1·925, 2·087, 2·133
$Cu_5V_2O_{10}$	1·934, 1·980	1·926, 2·042, 2·275
	1·895, 1·932	1·962, 2·038, 2·226

The VO_4 tetrahedra are slightly distorted with O–V(1)–O and O–V(2)–O angles varying from 107·8 to 113·1° and 104·8 to 112·9° respectively. The individual distances vary from the mean as might be expected from the fact that each tetrahedron contains one oxygen atom that is coordinated to only two cations (O(2) and O(5)) whereas the other oxygen atoms are coordinated to three or four cations. This results in the V(1)–O(2) and V(2)–O(5) distances being significantly shorter than the others. This dependence of V–O distances on the number and strength of the Cu–O bonds is evident from Table 6 where bond strengths around oxygen and consequent V–O distances have been calculated using Baur's (1970) method according to $d(V^{5+}–O)=1\cdot721+1\cdot602(\Delta p_0)$ (Gopal, 1972). Note that the short Cu–O bonds are given twice the weight of the long Cu–O bonds in the $Cu–O_6$ groups as suggested by Baur. The agreement is generally good except for V(1)–O(3), and substantially better than if these Cu–O bonds are given equal weight. A more systematic treatment of the effects due to varying Cu–O bond lengths is shown in Table 7 where Cu^{2+}–O bond

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* The degree of distortion is defined by $=\langle(\Delta R/\bar{R})^2\rangle$ where ΔR = difference of an individual distance from the mean value, $\bar{R}$.

strengths were calculated according to equation (1) recently derived from a large number of Cu–O distances (Brown & Shannon, 1973). The average discrepancy is reduced from 0·017 to 0·010 Å by the use of this relationship for the V(1)O_4 group and increased from 0·012 to 0·014 Å for the V(2)O_4 group. Although the predicted V(1)–O(3) bond length improves, however, it should be noted that this equation does not remove the discrepancy between the measured and calculated V(2)–O(8). Table 7 shows the strength(s) of all bonds in $Cu_5V_2O_{10}$ and the values for $\sum s_i$. Pauling's (1929) electrostatic-valence principle is valid to within an average deviation of about 3 % from the ideal values of 2·0 for Cu^{2+} and O^{2-} and 5·0 for V^{5+}.

The mean V–O distances within the two tetrahedra are 1·722 and 1·725 Å and agree well with a grand mean value of 1·721 ± 0·012 Å derived from 22 accurately refined vanadates (Gopal, 1972). The effective ionic radius of V^{5+} in $Cu_5V_2O_{10}$ (0·364 Å) obtained by subtracting the appropriate oxygen radius (Shannon, 1971) is significantly greater than that obtained in Na_3VO_4 $12H_2O$ (0·321 Å) (Tillmanns & Baur, 1970), Li_3VO_4 (0·337 Å) (Shannon & Calvo, 1973*b*), $Ba_3V_2O_8$ (0·317 Å) (Süsse & Buerger, 1970), Ca_2VO_4Cl (0·327 Å) (Banks, Greenblatt & Post, 1970), and $Ca_3V_2O_8$ (0·335 Å) (Gopal & Calvo, 1973). Similar behaviour was noted in $Cu_3V_2O_8$ (r = 0·365 Å). In ternary $M_xV_yO_z$ systems this behaviour is associated with the relative strengths of the M bonds; stronger bonds such as Cu^{2+}–O (as estimated from electronegativity or electrostatic bond strength criteria) result in longer average V^{5+}–O distances than weaker bonds such as Li^+–O, Na^+–O, Ca^{2+}–O or Ba^{2+}–O. This relationship has recently been discussed in greater detail for germanates (Shannon, 1971) and for phosphates, arsenates, and vanadates (Shannon & Calvo, 1973*b*).

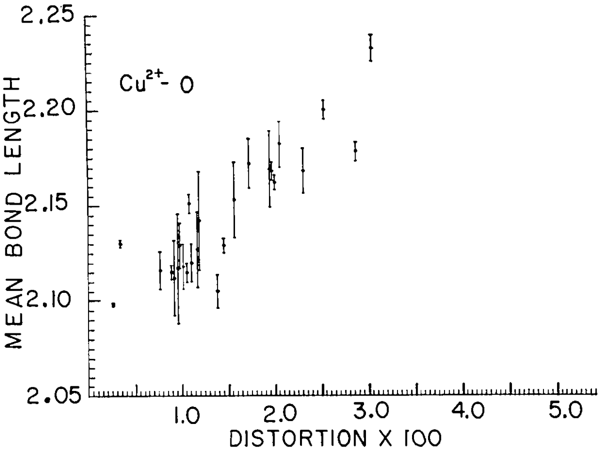

Fig. 3. Mean Cu^{2+}–O distance *vs.* distortion. Distortion is defined as $\langle(\Delta R/R)\rangle^2$ and vertical bars represent average e.s.d.'s quoted by authors.

Table 6. *Comparison of observed and predicted* V–O *bond lengths in* $Cu_5V_2O_{10}$

	p_0	Δp_0	s^*_{VO}	d_{obs}(Å)	$d†_{pred}$(Å)	$d‡_{pred}$(Å)
V(1)–O(1)	2·05	0·00	1·09	1·744	1·721	1·761
V(1)–O(2)	1·65	−0·40	1·49	1·658	1·657	1·656
V(1)–O(3)	2·25	+0·20	1·25	1·721	1·752	1·714
V(1)–O(4)	2·25	+0·20	1·03	1·764	1·752	1·780
Mean	2·05			1·722		
V(2)–O(5)	1·65	−0·45	1·44	1·650	1·649	1·667
V(2)–O(6)	2·45	+0·35	1·03	1·780	1·777	1·780
V(2)–O(7)	2·25	+0·15	1·19	1·728	1·745	1·731
V(2)–O(8)	2·05	−0·05	1·24	1·742	1·713	1·717
Mean	2·10			1·725		

* $s_{V-O} = 2·0 - \sum s_{O-Cu}$. The values of s_{O-Cu}. are taken from Table 7.
† $d_{pred} = 1·721 + 0·1602\ (\Delta p_0)$
‡ Calculated from $s_{V^{5+}} = 1·25\ (1·714/R)^{5·1}$, equation (2)

Table 7. *Bond strength*(*s*) *in* $Cu_5V_2O_{10}$*

	Cu(1)	Cu(2)	Cu(3)	Cu(4)	Cu(5)	V(1)	V(2)	$\sum s_{anion}$
O(1)			0·45		0·46	1·14		2·05
O(2)		0·51				1·48		1·99
O(3)	0·44	0·08			0·23	1·22		1·99
O(4)		0·45		0·16	0·38	1·08		2·07
O(5)					0·56		1·52	2·08
O(6)	0·37	0·40	0·20				1·03	2·00
O(7)		0·13	0·38	0·30			1·20	2·01
O(8)	0·13		0·50	0·13			1·15	1·90
O(9)	0·51		0·51	0·54	0·50			2·06
O(10)	0·54	0·51		0·54				
	0·06			0·32				1·97
$\sum s_{cat}$	2·05	2·09	2·04	1·99	2·13	4·93	4·90	

* $s_{Cu^{2+}} = 0·333\ (2·084/R)^{5·3}$, equation (1); $s_{V^{5+}} = 1·25\ (1·714/R)^{5·1}$, equation (2).

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Structure Cristalline du [(Pyridine-2,6 Dicarboxylato) (Acide Pyridine-2,6 Dicarboxylique)]-cuivre(II), Hydraté

PAR CHARLES SARCHET ET HENRI LOISELEUR

Laboratoire de Chimie Analytique II, *Université Claude Bernard Lyon* I, 43 *Boulevard du* 11 *Novembre* 1918, 9261-*Villeurbanne, France*

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[(Pyridine-2,6-dicarboxylato) (pyridine-2,6-dicarboxylic acid)]copper(II) hydrate crystallizes in space group *Pc* with cell parameters $a = 14{\cdot}76 \pm 0{\cdot}09$, $b = 10{\cdot}27 \pm 0{\cdot}03$, $c = 13{\cdot}76 \pm 0{\cdot}08$ Å, $\beta = 124{\cdot}0 \pm 0{\cdot}1°$ and $Z = 4$. The structure was determined by means of the Patterson function and Fourier syntheses, which were calculated from intensities collected on Weissenberg equi-inclination Cu $K\bar{\alpha}$ photographs. A group least-squares refinement lead to an *R* index of 0·10. The copper atom is octahedrally surrounded, being bonded to the nitrogen and two oxygen atoms of each tridentate ligand. The two orthogonal ligands coordinate in a different manner, one of them acting as anionic dipicolinate DP^{2-} and the other as neutral dipicolinic acid H_2DP. The copper atom is more tightly bonded to the DP^{2-} ligand. Each asymmetric unit involves six interstitial positions where hydrogen-bonded water molecules may be located.

Introduction

Le cuivre(II) forme avec l'acide pyridine-2,6 dicarboxylique H_2DP (acide dipicolique) plusieurs complexes cristallisés. Les structures cristallines de trois chélates 1:1 de formule $Cu(DP).nH_2O$ ont déjà été décrites (trihydrate monoclinique $P2/m$: Chastain, 1965; dihydrate monoclinique $P2_1/c$: Biagini Cingi, Chiesi Villa, Guastini & Nardelli, 1971; dihydrate triclinique $P\bar{1}$: Dominick, 1971; Sarchet, 1972). Il existe aussi une espèce 1:2 acide: $Cu(HDP)_2.xH_2O$ cristallisant soit seule à partir de solutions acides (par exemple $pH = 1$) soit simultanément avec les espèces 1:1 précédentes à partir de solutions de *p*H plus élevé (par exemple $pH = 4{,}5$). L'hydratation de ce chélate est variable, le cristal perd ou fixe de l'eau selon les conditions de préparation et de conservation. L'étude préliminaire par diffraction des rayons X montre cependant que l'édifice cristallin reste identique quel que soit le taux d'hydratation (Sarchet, 1972). La structure de ce chélate acide a été déterminée afin de pouvoir, en particulier, la comparer à celles des trois chélates 1:1 et à celle du bis(hydrogéno pyridine-2,6 dicarboxylato) nickel(II), trihydraté, établie par plusieurs auteurs (Gaw, Robin-