

## The Crystal Structure of a New Copper Wolfram Oxide, $\text{Cu}_3\text{WO}_6$

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The crystal structure of the previously unknown phase  $\text{Cu}_3\text{WO}_6$  has been determined and refined from X-ray, single crystal diffractometer data. The symmetry is cubic, space group  $Pa\bar{3}-T_h^6$  and the unit cell parameter  $a$  is  $9.797 (\pm 3) \text{ \AA}$ .

The structure can be described as composed of distorted  $\text{WO}_6$  octahedra and  $\text{CuO}_5$  triangular bipyramids which share corners and edges in a rather complicated way. Each octahedron is linked to 12 bipyramids and each bipyramid to 4 octahedra and 6 other  $\text{CuO}_5$  bipyramids.

Six  $\text{CuO}_5$  bipyramids sharing edges form a staggered ring with  $\bar{3}$  symmetry and one  $\text{WO}_6$  group on either side of the ring closes the hole in the centre. Interatomic distances and angles are given.

While many ternary oxide systems involving transition metals have been extensively studied especially in recent years, very little has been reported about the copper-wolfram-oxygen system. This is rather remarkable since the coordination chemistry of both these metals has drawn considerable attention and since there are inherent possibilities for interesting bonding features and physical properties in this system. There are a few papers in recent years reporting on " $\text{CuWO}_4$ ",<sup>1,2</sup>  $\text{Cu}_x\text{WO}_3$ ,<sup>3</sup> and  $\text{Cu}_x\text{WO}_{3+\delta}$ <sup>4</sup> but we have not found evidence in the literature for the existence of other intermediate phases in this system.

We have undertaken an investigation of this system by X-ray methods and in the course of this we have observed two phases, both prepared at about  $800^\circ\text{C}$ . A preliminary note about one of these, which we prefer to designate by the formula  $\text{CuWO}_{4-x}$ , but which is probably identical with the phases (phase) mentioned above, has recently been published in this journal.<sup>5</sup> Our studies on the second phase are reported in this article.

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## EXPERIMENTAL

Mixtures of CuO and WO<sub>3</sub> of analytical grade were placed in platinum tubes which were evacuated, sealed and heated for 3–5 days at 800°C. Oxygen deficient samples were prepared by substituting Cu<sub>2</sub>O or WO<sub>2</sub> for part of the copper(II) or wolfram(VI) oxide, respectively.

The samples were examined microscopically and by taking X-ray powder patterns in a Guinier-Hägg-type focusing camera using CuK $\alpha$ <sub>1</sub> radiation ( $\lambda=1.54051$  Å) and KCl as an internal standard ( $a[\text{KCl}, 20^\circ\text{C}]=6.2919$  Å<sup>3</sup>). The density was determined pycnometrically on one sample in duplicate runs.

Single crystal photographs were recorded in a Weissenberg camera using CuK $\alpha$  radiation. Data for the crystal structure determination were collected with a General Electric manual single crystal orienter equipped with a scintillation counter and using pulse height discrimination. MoK radiation filtered through a niobium foil and the  $\theta-2\theta$  scan technique were used in this case.

Diffractionometer settings were made for the 976 reflections with  $hkl \geq 0$  and  $\sin^2\theta \leq 0.20$ ; but after checking the peak intensity, the weakest reflections were rejected and only 653 were actually measured. The scan interval was calculated by the formula  $\Delta(2\theta) = 1.65 + 1.0 \times \tan\theta$  (degrees), the scan velocity was 0.4°/min in  $2\theta$  and the background was counted one minute at the beginning and end of each scan interval. After averaging the measured values for symmetry equivalent reflections, there remained a set of 234 non-equivalent intensity data which were used in the subsequent calculations.

IDENTIFICATION AND CHARACTERIZATION OF Cu<sub>3</sub>WO<sub>6</sub>

The powder patterns of samples with gross compositions around Cu<sub>3</sub>WO<sub>6</sub> indicated the presence of a new phase as a major component. The diffraction lines belonging to this phase could be indexed on the basis of a cubic unit cell with  $a \approx 9.79$  Å. It has not yet been possible to prepare it in a completely pure state but all samples made in this composition region, including those of stoichiometric composition, contained at least traces of CuO and/or CuWO<sub>4-x</sub> as demonstrated by their powder patterns. The cell constant  $a$  calculated from the powder patterns of different samples by least squares refinement falls within the range 9.7936( $\pm 2$ )–9.8005( $\pm 2$ ) Å (the errors given within parentheses are single sigma values for each individual pattern). Although no obvious relation between the sample composition and the cell parameter has been found, it cannot be excluded that these differences indicate the existence of a narrow homogeneity range for Cu<sub>3</sub>WO<sub>6</sub>.

A sample prepared from a mixture of 4CuO and WO<sub>3</sub> showed faint lines of CuO in addition to those of the new phase. The density of this sample was found to be  $\rho_{\text{obs}} = 6.62(\pm 10)$  g cm<sup>-3</sup>. The value calculated for Cu<sub>3</sub>WO<sub>6</sub> using the observed cell parameter and assuming eight formula units per cell is  $\rho_{\text{calc}} = 6.65$  g cm<sup>-3</sup>. Since the density of CuO is approximately 6.4 g cm<sup>-3</sup> a small amount of this compound as an impurity could not seriously affect the measured density value. It was therefore assumed that the unit cell content is Cu<sub>24</sub>W<sub>8</sub>O<sub>48</sub> which was proved to be correct by the subsequent structure analysis.

The Cu<sub>3</sub>WO<sub>6</sub> phase was formed as black, octahedrally shaped crystals and one of these was selected from a sample of stoichiometric composition for use in the single crystal studies. The powder pattern is listed in Table 1.

Table 1. X-Ray powder pattern of  $\text{Cu}_3\text{WO}_6$ . The values for the intensity of the lines have been obtained from rough visual estimation putting very strong=10 and very faint=1.  $\lambda=1.54051$  Å.  $\Delta=\sin^2\theta_{\text{obs}}-\sin^2\theta_{\text{calc}}$ .  $\sin^2\theta_{\text{calc}}$  based on  $a=9.7989(\pm 2)$  Å, calculated by least squares refinement.

<i>I</i>	$h^2+k^2+l^2$	$d_{\text{obs}}$	$\sin^2\theta_{\text{obs}} \times 10^5$	$\Delta \times 10^5$	<i>I</i>	$h^2+k^2+l^2$	$d_{\text{obs}}$	$\sin^2\theta_{\text{obs}} \times 10^5$	$\Delta \times 10^5$
9	3	5.660	1852	-1	8	41	1.5307	25320	-13
4	4	4.898	2473	1	4	42	1.5119	25954	2
10	5	4.385	3086	-3	9	45	1.4614	27780	-25
6	6	3.998	3711	3	9	46	1.4454	28399	-24
4	8	3.455	4971	27	2	48	1.4140	29672	12
4	9	3.265	5566	4	5	49	1.3998	30274	-2
6	11	2.954	6798	1	5	51	1.3725	31494	-18
10	13	2.7199	8020	-12	5	52	1.3590	32124	-6
10	14	2.6206	8639	-11	5	53	1.3462	32739	-9
8	16	2.4496	9887	0	9	54	1.3337	33352	-14
4	17	2.3766	10504	0	4	56	1.3098	34585	-17
6	18	2.3096	11122	0	4	57	1.2984	35193	-27
6	20	2.1906	12363	5	5	59	1.2756	36460	4
4	21	2.1384	12975	0	5	61	1.2546	37693	1
6	22	2.0900	13582	-11	5	62	1.2444	38313	3
3	25	1.9595	15451	3	3	64	1.2248	39546	0
2	26	1.9208	16081	15	1	65	1.2149	40196	32
6	27	1.8850	16697	13	2	66	1.2062	40780	-1
10	29	1.8194	17924	4	1	67	1.1967	41426	26
5	30	1.7888	18542	5	2	68	1.1880	42037	20
6	32	1.7317	19784	11	5	69	1.1795	42644	9
1	33	1.7057	20391	0	5	70	1.1710	43263	10
8	35	1.6562	21630	3	3	73	1.1468	45110	3
6	36	1.6323	22267	22	3	74	1.1389	45739	14
6	37	1.6105	22874	11	3	75	1.1314	46344	1
9	38	1.5895	23482	1	8	77	1.1169	47556	-22
4	40	1.5494	24713	-2	4	78	1.1098	48169	-26

#### DETERMINATION AND REFINEMENT OF THE STRUCTURE

The Laue symmetry  $m\bar{3}$  was evident in the Weissenberg photographs and from the observation of systematic absences of reflections the space group could be uniquely determined to be  $Pa\bar{3}-T_h^6$  (No. 205). The presence of both 8- and 24-fold positions in this space group was in accordance with the assumed composition and unit cell content.

A three-dimensional Patterson synthesis was calculated from the diffractometer data. Assuming the W atoms to occupy the 8-fold position  $x,x,x$ , a positional parameter could easily be found which gave rise to W-W vectors that could explain all the strong maxima in this synthesis. The W position, thus derived, was used in a difference Fourier synthesis from which plausible locations of the copper atoms in one 24-fold position were obtained. After a least squares refinement of the W and Cu positions, a second difference synthesis was calculated in which maxima corresponding to oxygen atoms were found. Least squares refinement of these atomic parameters was successfully performed and the resulting final parameters are given in Table 2.

Table 2. The crystal structure of  $\text{Cu}_3\text{WO}_6$ .

Space-group:  $Pa\bar{3}-T_h^8$   
 Unit cell parameter:  $a=9.797 (\pm 3) \text{ \AA}$   
 Unit cell content: 8  $\text{Cu}_3\text{WO}_6$

Atom	Position	$x$	$y$	$z$	$B$
W	8c	0.11703 ( $\pm 8$ )	$=x$	$=x$	0.19 ( $\pm 6$ )
Cu	24d	0.40443 ( $\pm 28$ )	0.24568 ( $\pm 26$ )	0.13762 ( $\pm 24$ )	0.69 ( $\pm 6$ )
O(1)	24d	0.2193 ( $\pm 13$ )	0.3016 ( $\pm 12$ )	0.0891 ( $\pm 12$ )	-0.13 ( $\pm 19$ )
O(2)	24d	0.4446 ( $\pm 15$ )	0.4636 ( $\pm 16$ )	0.1953 ( $\pm 16$ )	0.83 ( $\pm 24$ )

The errors given are the calculated single sigma values.

#### DETAILS OF THE CALCULATIONS

Computers of the types CD 3200, CD 3600, IBM 360/50, and IBM 1800 were used for the calculations. Among the programs used on these machines the following more important ones may be mentioned; PIRUM for indexing of powder patterns and refinement of cell constants (written by P.-E. Werner, Stockholm), GIP for calculation of diffractometer settings (R. Norrestam, Stockholm), DRF for data reduction and Fourier summations (A. Zalkin, Berkeley, Calif., USA, modified by R. Liminga and J.-O. Lundgren, Uppsala), LALS for full matrix least squares refinement (Gantzel-Sparks-Trueblood, Univ. of Calif., modified by A. Zalkin, J.-O. Lundgren, R. Liminga and C.-I. Brändén), DISTAN for calculation of interatomic distances, angles and standard deviations thereof (A. Zalkin, modified by J.-O. Lundgren and R. Liminga), and ORTEP for making stereo drawings (C. K. Johnson, Oak Ridge, Tenn., USA).

The crystal selected for the data collection was relatively large but its breadth varied only between 0.0107 cm and 0.0115 cm in all directions. Its shape, therefore, was considered a sphere in the absorption correction of the intensities. A linear absorption coefficient of  $\mu=397.5 \text{ cm}^{-1}$  was used in these calculations.

The atomic scattering factors used were those given for neutral Cu and W in Ref. 7 and for O in Ref. 8. The complex anomalous dispersion parameters given by Cromer<sup>9</sup> were applied on the scattering factors of Cu and W.

Weights in the least squares refinement were calculated according to the formula  $w=1/(7000+|F_{\text{obs}}|-0.3|F_{\text{obs}}|^2+0.45|F_{\text{obs}}|^3)$ . The weight analysis obtained in the last cycle is given in Table 3.

It became evident during the refinement that the strongest reflections suffered from extinction since the observed structure amplitudes for these were consistently smaller than the calculated values. The average of  $|F_{\text{obs}}|/|F_{\text{calc}}|$  was 0.80 for the 30 strongest reflections and these were given zero weight in the last few cycles of refinement. The final values of  $R=\sum||F_{\text{obs}}|-|F_{\text{calc}}||/\sum|F_{\text{obs}}|$  were 0.065 (the 30 strongest reflections omitted) and 0.120 (including the strong reflections).

The observed and calculated structure amplitudes are listed in Table 4.

Table 3. Weight analysis obtained in the last cycle of refinement.  $\Delta = ||F_{\text{obs}}| - |F_{\text{calc}}||$ ,  $w =$ weighting factor. The  $w\Delta^2$  values have been normalized.

Interval sin $\theta$	Number of independent reflections	$w\Delta^2$	Interval $ F_{\text{obs}} $	Number of independent reflections	$w\Delta^2$
0.000—0.209	24	1.411	0.0—57.2	20	1.707
0.209—0.263	22	0.502	57.2—72.7	20	0.943
0.263—0.301	22	0.732	72.7—89.1	21	1.167
0.301—0.332	24	1.160	89.1—102.1	20	0.638
0.332—0.357	20	1.213	102.1—119.2	21	0.926
0.357—0.379	24	1.044	119.2—135.7	20	0.409
0.379—0.400	20	1.290	135.7—154.4	20	0.738
0.400—0.418	13	0.661	154.4—178.8	21	1.079
0.418—0.434	21	1.216	178.8—205.1	20	0.944
0.434—0.450	13	0.769	205.1—260.2	21	1.449

Table 4. Observed and calculated structure amplitudes for  $\text{Cu}_3\text{WO}_6$ . The strong reflections which were considered to suffer considerably from extinction and therefore were given zero weight are marked by an asterisk.

h	k	l	$ F_{\text{obs}} $	$ F_{\text{calc}} $	h	k	l	$ F_{\text{obs}} $	$ F_{\text{calc}} $	h	k	l	$ F_{\text{obs}} $	$ F_{\text{calc}} $	h	k	l	$ F_{\text{obs}} $	$ F_{\text{calc}} $
0	2	0	150.4	142.2	5	5	1	221.4	232.0	7	8	2	243.9	252.7	8	8	4	246.0	270.6
0	10	0	140.3	120.9	5	6	1	178.9	186.6	8	3	2	73.4	77.2	10	5	4	116.2	125.5
0	12	0	184.5	193.7	5	7	1	134.1	132.8	8	6	2	69.9	64.8	11	0	4	74.7	85.9
2	2	0	88.5	80.2	5	9	1	193.2	190.0	9	4	2	98.2	87.1	5	5	5	214.9	196.3
2	4	0	217.8	231.8	5	10	1	138.4	145.0	9	5	2	183.5	183.2	5	6	5	230.7	231.8
2	6	0	72.7	75.4	6	2	1	207.0	222.5	9	7	2	161.0	181.8	5	7	5	104.1	96.9
2	9	0	62.0	57.3	6	3	1	156.2	151.9	11	5	2	60.2	55.6	5	9	5	209.8	213.0
4	1	0	137.9	135.3	6	5	1	105.8	108.3	1	4	3	33.4	25.6	5	10	5	136.1	139.6
4	3	0	112.6	114.6	6	6	1	133.1	126.6	3	3	3	119.5	116.8	6	7	5	59.1	64.5
4	4	0	230.8	262.5	6	7	1	111.6	103.0	3	5	3	102.1	100.7	6	9	5	176.8	171.9
4	5	0	159.7	155.9	6	8	1	63.7	65.9	3	6	3	193.0	204.4	7	6	5	154.6	151.6
4	10	0	191.8	207.5	6	9	1	135.8	143.9	3	7	3	82.4	77.6	7	8	5	174.5	165.2
6	1	0	260.3	283.6	6	10	1	99.9	99.4	3	9	3	109.0	108.9	8	6	5	158.8	159.7
6	2	0	197.3	204.2	7	2	1	163.7	158.6	3	10	3	133.4	141.5	1	9	6	44.2	30.0
6	5	0	202.3	198.6	7	3	1	122.7	123.3	4	4	3	183.9	204.7	6	6	6	112.3	107.7
6	6	0	20.0	27.0	7	4	1	57.2	47.7	4	6	3	266.2	226.8	6	7	6	162.2	170.1
6	8	0	224.9	246.6	7	5	1	89.0	75.7	4	7	3	51.6	48.3	7	7	6	166.9	135.3
6	10	0	109.6	106.7	7	6	1	141.6	136.8	4	8	3	231.8	269.8	7	8	6	250.6	265.0
8	3	0	163.1	130.3	7	8	1	131.9	131.2	4	10	3	129.3	131.2	8	3	6	61.7	68.4
8	5	0	178.6	180.5	7	9	1	123.6	110.1	5	5	3	190.4	205.3	2	4	7	51.4	41.2
8	6	0	113.2	102.9	7	10	1	142.1	134.9	5	6	3	120.5	113.6	2	6	7	54.3	41.5
10	1	0	250.6	269.1	8	2	1	193.3	191.4	5	7	3	89.6	90.1	2	8	7	72.3	61.2
10	2	0	96.7	88.3	8	3	1	88.3	87.3	5	9	3	117.6	109.0	5	4	7	57.6	56.8
10	4	0	61.4	55.6	8	5	1	141.9	132.4	5	10	3	102.2	103.1	9	2	7	95.6	101.4
10	5	0	121.9	129.6	8	6	1	183.0	189.6	6	5	3	255.7	285.1	7	5	8	52.5	52.9
10	6	0	138.9	130.6	8	9	1	111.6	98.0	6	6	3	142.8	155.7	7	4	9	64.5	69.3
12	2	0	107.9	105.1	9	3	1	110.9	102.1	6	9	3	223.9	246.4	9	7	9	94.4	86.8
1	2	1	106.4	94.3	9	5	1	196.7	215.3	6	10	3	119.2	118.0	3	2	11	52.9	43.5
1	3	1	154.5	157.6	9	7	1	101.8	94.6	7	4	3	70.0	68.2	0	4	0	376.9	551.2 *
1	4	1	167.7	174.1	10	2	1	134.1	139.8	7	5	3	72.5	64.0	1	1	1	196.2	263.0 *
1	5	1	192.5	200.4	10	3	1	100.7	95.3	7	6	3	142.2	139.2	2	1	0	250.5	324.5 *
1	6	1	106.5	89.2	10	4	1	84.4	86.2	7	9	3	89.2	82.0	0	6	0	319.8	373.6 *
1	7	1	101.5	94.6	10	5	1	127.6	121.7	8	3	3	51.0	54.2	0	8	0	400.9	501.2 *
1	8	1	126.5	121.0	10	6	1	68.5	57.0	8	4	3	93.1	91.7	2	3	0	362.6	715.7 *
1	9	1	153.1	150.9	10	7	1	109.4	117.6	8	5	3	81.3	69.2	2	5	0	279.8	349.5 *
1	10	1	96.5	88.6	12	2	1	81.5	76.4	8	7	3	98.9	101.9	2	7	0	307.6	351.2 *
1	12	1	96.6	101.6	0	4	2	111.8	64.3	8	8	3	122.9	118.6	2	11	0	335.2	390.6 *
2	2	1	65.2	59.3	2	2	2	8.0	5.8	9	5	3	144.8	159.2	4	6	0	295.8	398.5 *
2	3	1	132.2	135.9	2	3	2	69.7	74.2	9	7	3	80.5	77.9	4	0	2	283.7	347.5 *
2	4	1	43.8	34.5	2	7	2	75.7	67.1	10	5	3	230.0	254.9	6	3	0	361.6	507.0 *
2	5	1	79.7	74.5	2	9	2	115.6	106.0	0	6	4	47.5	43.6	6	7	0	289.7	340.1 *
2	6	1	65.2	66.4	2	10	2	71.3	69.0	1	3	4	36.6	28.5	8	4	0	369.7	477.8 *
2	7	1	175.8	192.5	3	3	2	203.4	246.7	1	5	4	34.5	35.7	8	0	0	305.9	349.0 *
2	8	1	90.1	87.1	3	5	2	156.4	155.9	1	11	4	50.2	47.7	10	3	0	264.4	279.8 *
2	9	1	136.9	144.3	3	6	2	166.9	170.1	4	4	4	108.4	103.0	10	7	0	270.0	285.0 *
2	11	1	141.3	138.8	3	7	2	159.9	170.9	4	5	4	100.7	96.4	3	2	1	275.2	427.8 *
3	3	1	63.6	57.0	3	11	2	171.2	194.7	4	6	4	132.1	133.3	3	6	1	270.1	341.1 *
3	5	1	186.3	200.1	4	4	2	80.0	79.1	4	8	4	250.9	296.9	5	2	1	264.7	332.1 *
3	7	1	82.1	77.7	4	6	2	90.3	85.1	5	7	4	84.7	78.2	11	2	1	257.9	381.3 *
3	8	1	45.0	46.0	5	7	2	194.5	189.3	5	8	4	75.8	75.7	3	4	2	266.4	352.0 *
3	9	1	111.1	117.9	5	8	2	209.0	221.1	5	9	4	84.1	80.0	3	8	2	350.1	464.2 *
3	10	1	205.2	228.4	6	3	2	145.0	153.4	6	5	4	202.9	214.8	5	3	2	340.2	506.9 *
4	2	1	78.3	69.4	6	4	2	138.2	144.1	6	6	4	123.6	126.5	5	4	2	281.0	359.9 *
4	4	1	47.0	47.8	6	5	2	62.6	59.0	6	7	4	151.7	159.3	5	5	2	261.1	308.7 *
4	5	1	90.6	94.1	6	9	2	78.2	71.9	6	8	4	195.3	192.6	5	11	2	264.4	277.1 *
4	6	1	94.5	88.3	6	9	2	115.4	109.4	6	9	4	120.5	122.8	9	3	2	269.5	303.1 *
4	9	1	54.1	60.1	7	4	2	133.4	129.0	8	5	4	154.5	159.8	11	4	2	268.9	317.1 *
4	10	1	172.5	194.1	7	6	2	206.7	210.1	8	7	4	80.0	73.9	8	6	3	292.4	334.9 *
5	3	1	177.4	188.1	7	7	2	187.1	182.5										

## DESCRIPTION AND DISCUSSION OF THE STRUCTURE

The structure of  $\text{Cu}_3\text{WO}_6$ , illustrated in Fig. 1, is of a type, which to our knowledge, has not been reported previously. It is quite different from the cubic or pseudocubic alkaline earth wolframates of the same stoichiometry which have

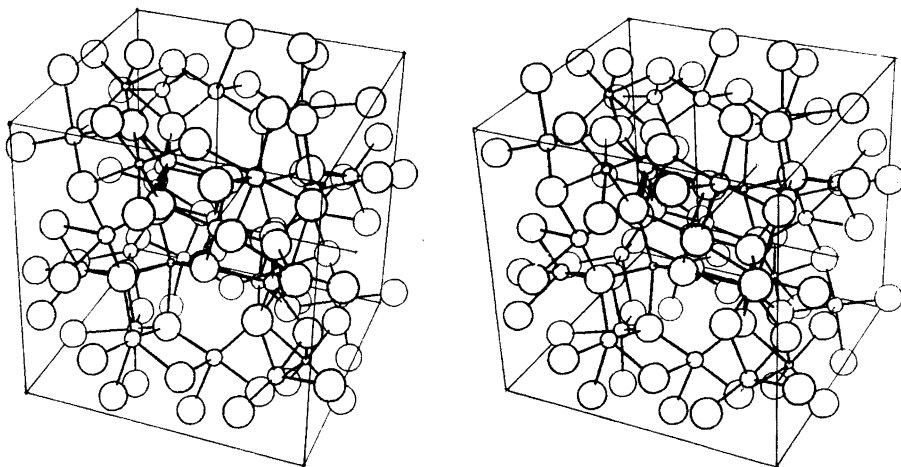


Fig. 1. A stereo pair showing the  $\text{Cu}_3\text{WO}_6$  structure. The metal atoms within one unit cell volume and their coordinating oxygen atoms are shown. The origin (0,0,0) is at the centre of the cube but is hidden behind a copper sphere. The positive directions of the axes from this point are indicated forming a right-handed coordinate system with  $z$  vertical. Small spheres = W, medium spheres = Cu, large spheres = O atoms.

long been known.<sup>10</sup> It can be considered as composed of distorted  $\text{WO}_6$  octahedra and  $\text{CuO}_5$  triangular bipyramids. These polyhedra are joined by shared corners or edges in a rather intricate way. Each  $\text{WO}_6$  octahedron is coupled to twelve  $\text{CuO}_5$  groups, to nine of these by corner-sharing and to the other three

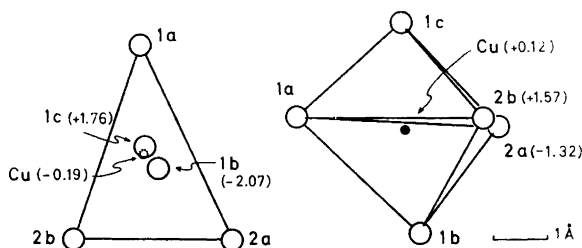
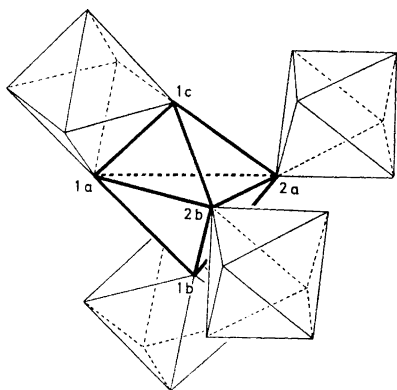
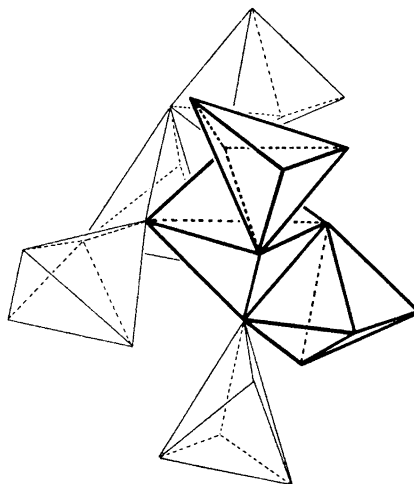


Fig. 2. The coordination of oxygen atoms around copper shown in two different projections. Left: Projection on the equatorial plane containing the oxygen atoms 1a, 2a and 2b. Right: Projection on the plane through 1a and the "poles" 1b and 1c. The values within parentheses are the distance in Å of the atoms above (+) or below (-) these planes.



*Fig. 3a.* The arrangement of  $\text{WO}_6$  octahedra around one  $\text{CuO}_5$  triangular bipyramid.

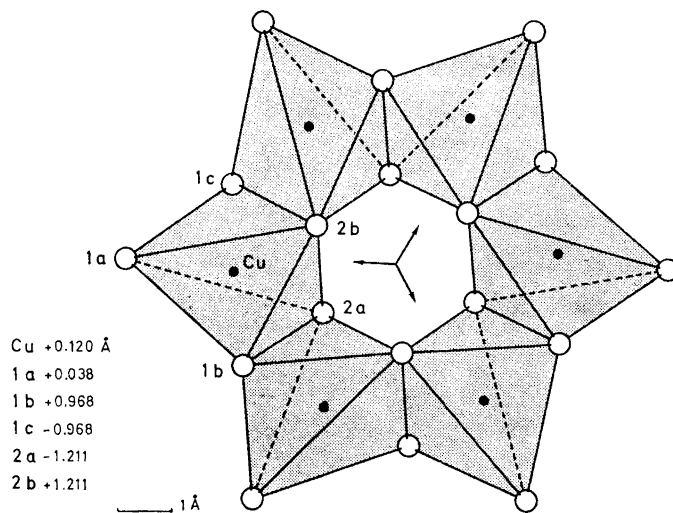


*Fig. 3b.* The arrangement of  $\text{CuO}_5$  bipyramids around one such group (the same as in *a* heavily indicated in the middle). The two adjacent bipyramids which belong to the same six-ring (Fig. 4) as the one in the middle have also been drawn with heavy lines.

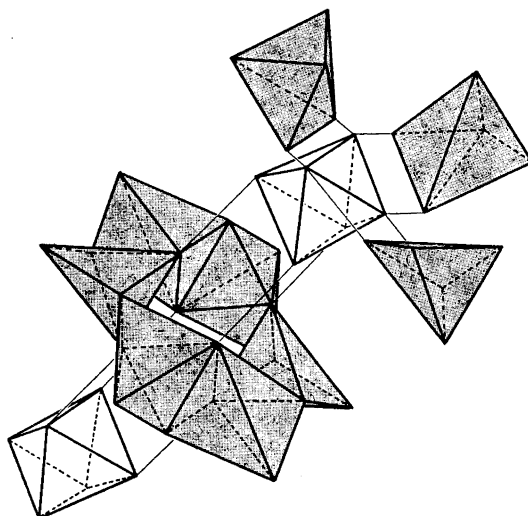
by edgesharing. The  $\text{WO}_6$  groups have no oxygen atoms in common although they occur pairwise in the structure with a separation of 3.97 Å between the wolfram atoms along the trigonal axes. Each  $\text{CuO}_5$  bipyramid, on the other hand, shares one of the non-equatorial edges (1a–1c, Fig. 2) with a  $\text{WO}_6$  octahedron and the three remaining corners with three other octahedra (Fig. 3a). It is also coupled to two other bipyramids by edge-sharing (1b–2a, 1c–2b) and to four additional bipyramids by corner-sharing (Fig. 3b).

Six mutually edge-sharing  $\text{CuO}_5$  bipyramids form a ring with the point group symmetry  $\bar{3}$  (Fig. 4) and such rings are centered on the equivalent positions  $4a$  of this space group  $(0,0,0; \frac{1}{2}, \frac{1}{2}, 0; 0, \frac{1}{2}, \frac{1}{2}; \frac{1}{2}, 0, \frac{1}{2})$ . The two  $\text{WO}_6$  octahedra which form a "pair" (*cf.* above) both share three corners with the same bipyramid ring and are situated on opposite sides of the plane (approximate, see below) of the ring on the trigonal axis (Fig. 5). The three edges of each octahedron connecting the corners which are not shared with the ring are shared with three other edges in three other bipyramid rings and the  $\text{WO}_6$  polyhedra may therefore be considered, formally, to act as a glue for the bipyramid rings.

Interatomic distances and bond angles are listed in Table 5. As was mentioned above, the octahedral coordination around wolfram is not regular but distorted so that only one of the threefold axes remains of the point group symmetry elements. This gives rise to three short and three long W–O bonds and may be looked upon as resulting from a displacement of the metal atom from the centre towards one of the octahedral faces. This 3+3 type coordina-



*Fig. 4.* The arrangement of six  $\text{CuO}_6$  bipyramids to form a ring of the trigonal symmetry  $\bar{3}$  viewed along the trigonal axis. The level of the atoms in Å above (+) or below (-) the plane through the inversion centre is given to the left. One  $\text{WO}_6$  octahedron above the ring is connected to it through the oxygen atom 2b and its 3-fold related equivalents and an equivalent octahedron below the plane connected through the oxygen 2a and its two equivalents.



*Fig. 5.* The connection of two  $\text{WO}_6$  octahedra (related by an inversion centre) to a bipyramid ring, each by three shared corners. The coupling of one of the octahedra to bipyramids in three different rings by shared edges is also indicated.



tion seems not to have been reported previously for any wolfram-oxygen compound in which the W—O distances have been determined with sufficient accuracy. Hexavalent wolfram is often tetrahedrally coordinated by oxygen but distorted octahedral coordination is also rather common. It occurs for example in  $\text{WO}_3$  and in ternary oxides of the wolframite type (for instance  $\text{NiWO}_4$ ,<sup>11</sup>  $\text{CdWO}_4$ ,<sup>12</sup> and  $\text{CuWO}_{4-x}$ <sup>5</sup>). In most of these cases the distortion gives rise to a group of four shorter and two longer bonds and can be regarded as reflecting a tendency towards four-coordination.

There is no doubt concerning the coordination number for copper in  $\text{Cu}_3\text{WO}_6$ . The five nearest oxygen atoms are within 2.25 Å while the next nearest oxygen is 3.10 Å from the Cu atom. The details of coordination should be evident from Table 5 and Figs. 2 and 3. It is seen that the deviation from regularity is predominantly a relaxation of the trigonal symmetry giving rise to one short and two long edges in the equatorial plane.

The most common coordination around bivalent copper seems to be the four-fold, square planar arrangement with or without two more distant ligands completing a distorted octahedron. Five-fold coordination has also been observed in a few structures, especially metal-organic compounds. In most of these latter cases the coordination figure is best described as a square pyramid but in a few structures, including the present one, it must be regarded as a triangular bipyramid. These are  $\text{Cu}_2(\text{OH})\text{AsO}_4$  (olivenite)<sup>13</sup> and the isomorphous  $\text{Cu}_2(\text{OH})\text{PO}_4$  (libethenite),<sup>14</sup>  $\text{Cu}_2\text{O}(\text{SO}_4)$  (dolerophanite),<sup>15</sup>  $[\text{Cr}(\text{NH}_3)_6]\text{CuCl}_5$ ,<sup>16</sup> and  $\mu_4$ -oxohexa- $\mu$ -chlorotetrakis(triphenylphosphine oxide) copper(II).<sup>17</sup> In the first three only one half of the copper atoms are five-coordinated, the other half of them have 4+2 bonding.

The shortest distance between copper atoms is that between the atoms situated in two bipyramids that share an edge, *i.e.* the distance between adjacent copper atoms in the rings. This distance, 2.990(±3) Å, may be compared with the closest approach of metal atoms in CuO, where the three shortest distances are 2.9005(±3), 3.0830(±4) and 3.1734(±4) Å according to a recent refinement.<sup>18</sup> The present value, which occurs twice for each copper atom, is seen to be almost exactly the mean of the two shortest distances in CuO. Corresponding distances in  $\text{CuWO}_{4-x}$  are 2.986(±2) Å and 3.150(±2) Å.<sup>19</sup>

The oxygen-oxygen distances are quite normal throughout; see Table 5. A shortening of the O—O distances along edges which are common to two polyhedra is a generally observed phenomenon in structures where there is no appreciable metal-metal interaction across these edges. This effect is noticeable also in this structure as the shortest edges within each polyhedron are those shared with other polyhedra. It is less pronounced for edges shared between two  $\text{CuO}_5$  bipyramids (1c—2b, 1b—2a, Fig. 3) than for those shared between a bipyramid and a  $\text{WO}_6$  octahedron (1a—1c) in accordance with the rules developed by Pauling from simple electrostatic arguments.

The "oxygen volume",  $V_{\text{cell}}/n_{\text{O}}$ , is 19.57 Å<sup>3</sup> which indicates a fairly open oxygen lattice. Corresponding values for structures with small cations in a close packed oxygen framework usually lie within the range 16.0—16.5 Å<sup>3</sup>. An open lattice is also indicated since the oxygen atoms have only nine oxygen near neighbours, lying within a distance of 3.10 and 2.92 Å, whereas the

Table 5. Interatomic distances and angles in  $\text{Cu}_3\text{WO}_6$ .

		<i>Within octahedra</i>		Distance between the oxygen atoms
W—O(2) (3×)	1.791 (±16) Å	O(1)—W—O(1) (3×)	76.1 (±5)°	2.57 (±2) Å
—O(1) (3×)	2.085 (±12)	O(1)—W—O(2) (3×)	88.6 (±6)	2.72 (±2)
		O(1)—W—O(2) (3×)	89.3 (±6)	2.73 (±2)
		O(2)—W—O(2) (3×)	102.7 (±6)	2.80 (±2)
		O(1)—W—O(2) (3×)	161.0 (±6)	3.82 (±2)
<i>Within bipyramids</i>				
Cu—O(1b)	1.921 (±12) Å	O(1c)—Cu—O(1a)	81.1 (±7)°	2.57 (±2) Å
—O(1c)	1.953 (±13)	O(1c)—Cu—O(2b)	87.7 (±6)	2.78 (±2)
—O(1a)	2.002 (±12)	O(1c)—Cu—O(2a)	87.5 (±5)	2.91 (±2)
—O(2b)	2.060 (±15)	O(1b)—Cu—O(1a)	104.3 (±3)	3.10 (±2)
—O(2a)	2.243 (±16)	O(1b)—Cu—O(2b)	93.3 (±6)	2.90 (±2)
		O(1b)—Cu—O(2a)	83.4 (±5)	2.78 (±2)
		O(1a)—Cu—O(2a)	135.8 (±6)	3.93 (±2)
		O(1a)—Cu—O(2b)	136.3 (±6)	3.77 (±2)
		O(2a)—Cu—O(2b)	85.1 (±8)	2.91 (±2)
		O(1b)—Cu—O(1c)	170.8 (±5)	3.86 (±2)
<i>Between polyhedra</i>				
W—W	3.970 (±1) Å	O(1)—Cu	1.921 (±12) Å	
—Cu (3×)	3.090 (±3)	—Cu	1.953 (±13)	
—Cu (3×)	3.420 (±3)	—Cu	2.002 (±12)	
—Cu (3×)	3.516 (±3)	—W	2.085 (±12)	
—Cu (3×)	3.648 (±3)			
		O(2)—W	1.791 (±16)	
Cu—W	3.090 (±3)	—Cu	2.060 (±15)	
—W	3.420 (±3)	—Cu	2.243 (±16)	
—W	3.516 (±3)	—O(2) (2×)	3.59 (±3)	
—W	3.648 (±3)			
—Cu (2×)	2.990 (±3)			
—Cu (2×)	3.219 (±4)			
—Cu (2×)	3.529 (±3)			

next nearest neighbours are not closer than 3.93 and 3.59 Å for O(1) and O(2), respectively.

This compound, which has crystallographically equivalent copper atoms in a somewhat unusual coordination with oxygen, should be studied by other methods, and investigations of its electric and magnetic properties have been started at this Institute. In this connection a closer examination of possible non-stoichiometry will also be made. Preliminary measurements (made by G. Barvling and L. Kihlberg) indicate that  $\text{Cu}_3\text{WO}_6$  exhibits temperature independent paramagnetism over the range 120–290°K with the value  $\chi_g = 4.5 \times 10^{-6}$  cgs units.

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## REFERENCES

1. Van Uitert, L. G., Rubin, J. J. and Bonner, W. A. *J. Am. Ceram. Soc.* **46** (1963) 512.
2. Clark, G. M. and Doyle, W. P. *Spectrochim. Acta* **22** (1966) 1441.
3. Conroy, L. E. and Sienko, M. J. *J. Am. Chem. Soc.* **79** (1957) 4048.
4. Sienko, M. J. and Weller, P. F. *Inorg. Chem.* **1** (1962) 324.
5. Gebert, E. and Kihlberg, L. *Acta Chem. Scand.* **21** (1967) 2575.
6. Hambling, P. G. *Acta Cryst.* **6** (1953) 98.
7. Cromer, D. T. and Waber, J. T. *Acta Cryst.* **18** (1965) 104.
8. Hanson, H. P., Herman, F., Lea, J. D. and Skillman, S. *Acta Cryst.* **17** (1964) 1040.
9. Cromer, D. T. *Acta Cryst.* **18** (1965) 17.
10. Steward, E. G. and Rooksby, H. P. *Acta Cryst.* **4** (1951) 503.
11. Keeling, Jr., R. O. *Acta Cryst.* **10** (1957) 209.
12. Chichagov, A. P., Ilyukhin, V. V. and Belov, N. V. *Dokl. Akad. Nauk SSSR* **166** (1966) 87.
13. Heritsch, H. Z. *Krist.* **99** (1938) 466.
14. Walitzi, E. M. *Mineral. Petrogr. Mitt.* **8** (1963) 614.
15. Flügel-Kahler, E. *Acta Cryst.* **16** (1963) 1009.
16. Mori, M., Saito, Y. and Watanabe, T. *Bull. Chem. Soc. Japan* **34** (1961) 295.
17. Bertrand, J. A. *Inorg. Chem.* **6** (1967) 495.
18. Åsbrink, S. and Norrby, L.-J. *To be published.*
19. Kihlberg, L. and Gebert, E. *To be published.*

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