

The Crystal Structure of Copper Uranium Tetroxide*

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Copper monouranate crystallizes in the monoclinic system with $a=5.475 \pm 0.006$, $b=4.957 \pm 0.006$, $c=6.569 \pm 0.006$ Å and $\beta=118.87^\circ \pm 0.15^\circ$. The space group is $P2_1/n$ with two formula weights in the cell. The uranium–oxygen configuration is characterized by short collinear uranyl bonds, each of length 1.90 Å, nearly normal to a planar and almost square array of secondary uranium–oxygen bonds of lengths 2.15 and 2.24 Å. Two uranyl and two secondary oxygen atoms form a square planar configuration about each copper atom with copper–oxygen bond lengths of 1.95 and 1.96 Å. Two very long copper–oxygen bonds, of lengths 2.59 Å each are observed above and below the copper–oxygen plane. All bond distances are consistent with bond strength values.

Introduction

Uranates of the 3d transition metals from chromium and including zinc have been found to exist in three structural modifications. $MnUO_4$, $CoUO_4$, β - $NiUO_4$, and $ZnUO_4$ belong to the $MgUO_4$ structure type, $CrUO_4$, $FeUO_4$, and α - $NiUO_4$ probably belong to the $BiVO_4$ type, and $CuUO_4$ is the third form which has been observed. The preparation of $CuUO_4$ has been described by Brisi (1963) who reported only d -spacings from a powder pattern.

Copper monouranate was prepared by the reaction of the component oxides and the single crystals were grown by hydrothermal techniques. Details covering the preparative methods and an examination of the properties of these and other double oxides have already been described. (Hoekstra & Marshall, 1967).

Crystallographic data

Copper monouranate crystallizes in the monoclinic system. The cell, determined from rotation, Weissenberg, and precession data with $Cu K\alpha$ ($\lambda=1.5417$ Å) and $Mo K\alpha$ (0.71069 Å) radiation has the following dimensions: $a=5.475 \pm 0.006$, $b=4.957 \pm 0.006$, $c=6.569 \pm 0.006$ Å; $\beta=118.87^\circ \pm 0.15^\circ$. The calculated density based on two molecules in the cell is 7.77 g.cm^{-3} which may be compared with the observed value of 7.6 g.cm^{-3} .

Reflections hkl show no systematic absences, but reflections $h0l$ are absent unless $h+l=2n$ and reflections $0k0$ are absent unless $k=2n$. The space group is therefore taken as $P2_1/n$ (C_{2h}^2). The possible atomic positions for this space group are: fourfold, $\pm x, y, z$; $\pm(\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z)$; twofold, $000, \frac{1}{2}\frac{1}{2}\frac{1}{2}; \frac{1}{2}00, 0\frac{1}{2}\frac{1}{2}; 00\frac{1}{2}, \frac{1}{2}\frac{1}{2}0$; and $\frac{1}{2}0\frac{1}{2}, 0\frac{1}{2}0$.

The linear absorption coefficient for $CuUO_4$, based on $Mo K\alpha$ radiation, is 844 cm^{-1} , an indication that considerable care must be exercised in correcting for this large absorption effect. The crystals are rhombic in appearance, but intensity data collected from very small crystals of this general shape proved to be so unsatisfactory that it was necessary to record diffraction data from a sphere. Crude spheres only could be prepared because of cleavage; however, one of diameter 0.077 ± 0.005 mm was found to produce reliable intensity information.

Intensity data were collected with a single-crystal orienter mounted on a General Electric XRD-5 diffraction unit. The entire hemisphere for reflections up to $2\theta=53^\circ$ was investigated, using $Mo K\alpha$ radiation. The reflections were maximized, and intensity readings were obtained with balanced filters, the numerical values being taken as the difference in readings for the two filters. Lorentz, polarization, and absorption corrections were applied in the usual manner.

Determination of the structure

All reflections for which $h+k+l=2n$ are strong, indicating that the uranium atoms are in positions $000, \frac{1}{2}\frac{1}{2}\frac{1}{2}$. Bond distance considerations then lead to $00\frac{1}{2}, \frac{1}{2}\frac{1}{2}0$ as probable copper atom positions.

Initially, a three-dimensional Fourier synthesis was prepared using the uranium positions at 000 and $\frac{1}{2}\frac{1}{2}\frac{1}{2}$. This was based on a modified Sly and Shoemaker program, *Two- and Three-Dimensional Crystallographic Fourier Summation Program for the IBM 704 Computer*. In addition to the uranium atoms, copper peaks appeared at positions $00\frac{1}{2}$ and $\frac{1}{2}\frac{1}{2}0$. A set of very weak maxima was also observed and these could be attributed to the oxygen atoms. Additional oxygen coordinates corresponding to the apparent centering were eliminated on the basis of acceptability of the bond distances and reasonableness of the derived configurations.

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A difference synthesis was then carried out with the uranium and copper contributions removed from the observed structure factors. Atomic scattering curves used in computing the structure factors for the metal atoms were based on values given in *International Tables for X-ray Crystallography* (1962). The anomalous dispersion correction of $\Delta f' = -9.19$ and $\Delta f'' = 9.09$ electrons for uranium, reported by Cromer (1965), was included in evaluating the uranium contribution. Reflections with strong intensities arise from the metal and oxygen positions, while the weak reflections, for which the sum $h+k+l$ is odd, depend on the oxygen coordinates only. The imaginary part of the dispersion

correction therefore produces a negligible effect and was accordingly not considered in the refinement.

The Busing, Martin & Levy *Fortran Crystallographic Least Squares Program* was used in order to establish an absolute scale for the observed data and to introduce temperature factors. Following appropriate scaling, the three-dimensional difference Fourier synthesis was carried out and this led to the formation of very distinct oxygen peaks at positions previously noted. The contribution of the oxygen atoms, based on these positions and the O^{2-} atomic scattering curve of Tokonami (1965), was added to the uranium and copper scattering to derive F_{cal} . for a least-squares

Table 1. *Position parameters and temperature factors*

	Cu	U	O(1)	O(2)
x	0	0	0.1721 (24)	0.2700 (26)
y	0	0	0.1806 (27)	-0.2958 (30)
z	0.5	0	0.3389 (20)	0.5858 (22)
$B(\text{\AA}^2)$	—	—	1.40 (23)	2.01 (27)
β_{11}	0.0150 (12)	0.0077 (4)	—	—
β_{22}	0.0071 (12)	0.0038 (4)	—	—
β_{33}	0.0107 (9)	0.0045 (3)	—	—
β_{12}	0.0006 (10)	0.0000 (3)	—	—
β_{13}	0.0080 (9)	0.0029 (2)	—	—
β_{23}	-0.0001 (8)	-0.0001 (2)	—	—

Table 2. *Observed and calculated structure factors*

h k l	0.8F _o	0.8F _c	h k l	0.8F _o	0.8F _c	h k l	0.8F _o	0.8F _c	h k l	0.8F _o	0.8F _c	h k l	0.8F _o	0.8F _c
0 2 0	186.5	119.5	-2 3 1	60.1	58.4	-2 2 2	132.5	141.2	-2 3 3	65.5	63.7	-2 5 4	< 2.0	0.3
0 4 0	110.6	104.8	2 4 1	3.7	-1.8	2 3 2	3.9	4.3	2 4 3	7.7	7.2	3 1 4	73.5	73.9
0 6 0	75.4	75.9	-2 4 1	8.0	1.2	-2 3 2	6.8	5.7	-2 3 4	< 2.5	-0.5	-3 1 4	100.7	121.5
1 1 0	150.9	165.9	2 5 1	39.4	40.4	2 4 2	80.2	81.7	-2 5 3	41.6	42.3	3 2 4	< 2.0	0.8
1 2 0	84.6	-20.0	-2 5 1	45.2	46.4	-2 4 2	90.5	94.7	3 0 3	39.9	40.1	-3 2 4	8.1	7.3
1 3 0	116.9	113.7	3 0 1	61.6	61.0	2 5 2	< 2.7	-0.2	-3 0 3	65.8	66.0	-3 3 4	85.8	87.5
1 4 0	14.9	12.1	-3 0 1	78.2	77.6	-2 5 2	3.3	2.4	3 1 3	< 4.7	-1.0	-3 4 4	6.4	-4.6
1 5 0	88.8	87.2	3 1 1	14.4	12.5	3 1 2	96.1	96.0	-3 1 3	5.3	-3.9	-3 5 4	74.3	75.9
1 6 0	2.7	-4.7	-3 1 1	2.5	-1.2	3 2 1	128.4	133.5	3 2 3	55.1	56.2	-4 0 4	103.9	102.1
2 0 0	119.6	117.6	3 2 1	59.0	59.2	3 2 2	6.6	-4.7	-3 2 3	60.5	60.3	-4 1 4	16.7	15.4
2 1 0	19.7	-17.3	-3 2 1	59.2	58.0	-3 2 2	14.0	-11.1	3 3 3	< 2.9	1.0	-4 2 4	101.6	100.8
2 2 0	138.6	141.9	3 3 1	3.2	-3.5	3 3 2	84.3	84.2	-3 3 3	< 2.9	1.4	-4 3 4	6.2	-4.3
2 3 0	5.7	3.2	-3 3 1	3.1	2.7	-3 3 2	92.6	95.1	-3 4 3	51.6	52.1	-4 4 4	78.5	77.8
2 4 0	94.4	92.7	3 4 1	44.7	44.7	3 4 2	3.0	3.7	-3 5 3	< 1.0	-0.2	-5 1 4	87.1	86.7
2 5 0	4.1	1.9	-3 4 1	50.2	49.7	-3 4 2	9.4	9.1	4 1 3	42.4	42.9	-5 2 4	< 2.0	0.4
3 1 0	115.6	112.3	-3 5 1	3.7	-2.9	-3 5 2	76.3	80.1	-4 1 3	57.1	58.4	-5 3 4	87.2	86.7
3 2 0	6.5	5.2	4 1 1	56.3	56.6	4 0 2	78.5	77.3	4 2 3	< 2.0	5.1	-5 4 4	< 2.0	0.7
3 3 0	108.2	106.4	-4 1 1	60.8	58.7	-4 0 2	126.0	131.1	-4 2 3	2.1	-2.0	-5 0 4	76.6	75.6
3 4 0	3.6	-4.9	4 2 1	< 2.0	1.9	4 1 2	3.8	0.9	-4 3 3	50.0	51.9	-6 1 4	8.3	-8.7
3 5 0	87.0	68.0	-4 2 1	4.8	4.9	-4 1 2	5.6	5.7	-4 4 3	< 2.0	0.7	-6 2 4	76.2	75.3
4 0 0	107.3	104.6	4 3 1	40.3	39.4	4 2 2	76.2	77.8	-4 5 3	38.3	39.9	0 1 5	54.6	53.5
4 1 0	11.6	10.4	-4 3 1	52.0	49.8	-4 2 2	91.3	90.5	-5 0 3	49.8	51.4	0 2 5	4.6	6.5
4 2 0	90.1	89.2	4 4 1	< 2.7	-1.8	4 3 2	< 2.0	-1.7	-5 1 3	1.9	-2.1	0 3 5	53.3	54.3
4 3 0	3.6	-3.3	-4 4 1	5.0	-4.3	-4 3 2	4.1	-1.7	-5 2 3	50.3	51.0	0 4 5	5.8	-5.4
4 4 0	74.2	75.2	5 0 1	50.6	51.4	-4 4 2	79.5	80.2	-5 3 3	< 2.9	-0.6	1 0 5	59.6	59.5
5 1 0	83.9	80.8	-5 0 1	46.1	44.8	-5 1 2	90.9	91.3	-5 4 3	38.1	39.4	-1 0 5	47.6	46.2
5 2 0	< 2.0	0.9	5 1 1	3.9	-6.0	-5 2 2	11.6	7.5	-6 0 3	< 2.0	< 0.1	1 1 5	13.0	9.7
5 3 0	65.1	65.0	-5 1 1	6.2	4.8	-5 3 2	78.1	77.2	-6 1 3	44.3	46.1	-1 1 5	6.0	-5.5
6 0 0	87.4	87.1	5 2 1	39.0	38.7	-6 0 2	68.5	68.0	-6 2 3	< 2.0	-1.5	1 2 5	44.6	45.7
6 1 0	83.5	83.0	-5 2 1	51.7	51.1	-6 1 2	3.2	2.6	0 0 4	108.6	103.4	-1 2 5	65.3	63.9
6 2 0	5.2	-6.4	-5 3 1	4.2	-2.7	-6 2 2	74.8	75.5	0 1 4	< 1.4	0.5	1 3 5	3.7	-3.3
6 3 0	65.9	63.4	5 4 1	40.9	40.5	0 1 3	77.9	75.8	0 2 4	112.8	112.0	-1 3 5	3.9	51.9
6 4 0	2.7	3.1	-5 4 1	2.0	150.3	0 2 3	5.5	5.0	0 3 4	4.0	-1.7	-1 4 5	45.4	45.7
6 5 0	53.4	49.8	0 1 2	33.2	32.1	0 3 3	50.6	50.7	0 4 4	81.0	81.5	2 1 5	48.8	50.1
0 5 1	< 2.0	< 0.1	0 2 2	129.0	131.0	0 4 3	5.1	-4.1	0 5 4	< 2.0	2.5	-2 1 5	61.4	59.4
1 0 1	73.6	71.5	0 3 2	9.7	-7.4	0 5 3	49.0	48.3	1 1 4	101.2	99.0	2 2 5	2.7	-1.2
-1 0 1	81.1	89.2	0 4 2	100.5	98.9	1 0 3	80.9	83.1	-1 1 4	125.7	120.2	-2 2 5	7.2	-7.5
1 1 1	131.4	135.5	0 5 2	3.2	-1.8	-1 0 3	75.2	66.8	1 2 4	2.9	3.5	-2 3 5	53.4	54.9
-1 1 1	4.0	2.0	1 1 2	135.4	142.1	-1 1 3	16.2	13.5	-1 2 4	10.8	-8.8	-2 4 5	7.5	6.4
1 2 1	72.6	72.2	-1 1 2	146.5	139.0	-1 1 3	16.2	13.5	1 3 4	87.2	88.0	-3 0 5	73.3	70.0
-1 2 1	69.5	72.8	1 2 2	5.8	5.3	1 2 3	52.6	51.3	-1 3 4	106.5	100.5	-3 1 5	2.4	-1.9
1 3 1	5.6	4.7	-1 2 2	7.4	5.2	-1 2 3	76.9	72.0	1 4 4	2.6	-3.0	-3 2 5	48.8	48.4
-1 3 1	4.6	-3.7	1 3 2	95.4	95.8	1 3 3	2.8	1.2	-1 4 4	13.0	7.4	3 3 5	3.5	-3.0
1 4 1	56.7	57.2	-1 3 2	140.8	131.9	-1 3 3	3.6	-2.3	-1 5 4	70.5	72.0	-3 4 5	45.6	45.8
-1 4 1	51.8	54.0	1 4 2	4.1	-3.1	1 4 3	52.2	50.6	-2 0 4	92.9	91.4	-4 1 5	56.0	56.5
1 5 1	< 2.0	-0.5	-1 4 2	2.8	-3.2	-1 4 3	51.9	49.5	-2 0 4	146.5	143.6	-4 2 5	3.0	2.5
-1 5 1	5.5	5.8	1 5 2	82.0	83.5	1 5 3	< 2.7	2.5	2 1 4	3.9	2.0	-4 3 5	43.9	44.1
-1 6 1	38.9	42.5	-1 5 2	75.3	75.6	-1 5 3	< 2.7	-2.1	-2 1 4	13.9	-11.3	-4 4 5	< 2.0	-2.6
2 1 1	85.9	84.0	2 0 2	127.3	128.6	2 1 3	55.9	56.8	2 2 4	79.4	80.1	-5 0 5	48.2	48.2
-2 1 1	78.5	78.0	-2 0 2	121.2	125.8	-2 1 3	69.6	66.4	-2 2 4	109.7	103.2	-5 1 5	6.3	2.4
2 2 1	5.6	3.9	2 1 2	13.3	-11.6	2 2 3	7.2	-7.7	2 3 4	< 2.0	0.7	-5 2 5	49.6	48.7
-2 2 1	2.7	-1.8	-2 1 2	26.4	-26.6	-2 2 3	3.4	2.0	-2 3 4	6.1	4.8	-5 3 5	2.6	0.1
2 3 1	66.5	65.3	2 2 2	102.7	102.5	2 3 3	53.7	53.1	-2 4 4	88.7	86.3	-6 1 5	43.4	42.8

refinement. A final least-squares analysis led to a reliability index R of 4%, with $R = \sum ||F_o| - |F_c|| / \sum |F_o|$. The coordinates obtained from this refinement are presented in Table 1. Observed and calculated structure factors are listed in Table 2.

Discussion of the structure

A perspective view of the structure is shown in Fig. 1. The general features indicate a uranium atom surrounded by four secondary oxygen atoms with a collinear uranyl bond normal to the plane of the secondary configuration. Similarly, each copper atom is surrounded by four oxygen atoms with two long copper-oxygen bonds more or less normal to this array. A listing of bond distances and bond angles is presented in Table 3.

The array of the four secondary oxygen atoms about a uranium atom is planar by symmetry. The equivalent

$U(1)-O(1)$ and $U(1)-O(1')$ distances are 2.15 Å, while $U(1)-O(1'')$ and $U(1)-O(1''')$ are 2.24 Å. The uranyl configuration $O(2'')-U(1)-O(2''')$ is collinear by symmetry with uranyl bond lengths of 1.90 Å for $U(1)-O(2'')$ and $U(1)-O(2''')$. The uranyl bond makes angles of 86.4° and 91.2° with the secondary bonds. The secondary oxygen-oxygen distances are: $O(1')-O(1'')$, and $O(1''')-O(1)$, 3.03 Å, and $O(1')-O(1''')$ and $O(1)-O(1'')$, 3.17 Å. These secondary oxygen bonds form a slightly distorted square with included angles of 87.7° and 92.3° . It is evident that, to a first approximation, the configuration is represented by uranyl bonds normal to a square planar array of secondary uranium-oxygen bonds.

In a similar manner, the oxygen configuration about a copper atom and including the copper atom, is planar by symmetry. All copper-oxygen bonds are 1.95 and 1.96 Å in length and hence, are equal within experimental error. As indicated in Fig. 1, the oxygen-oxygen

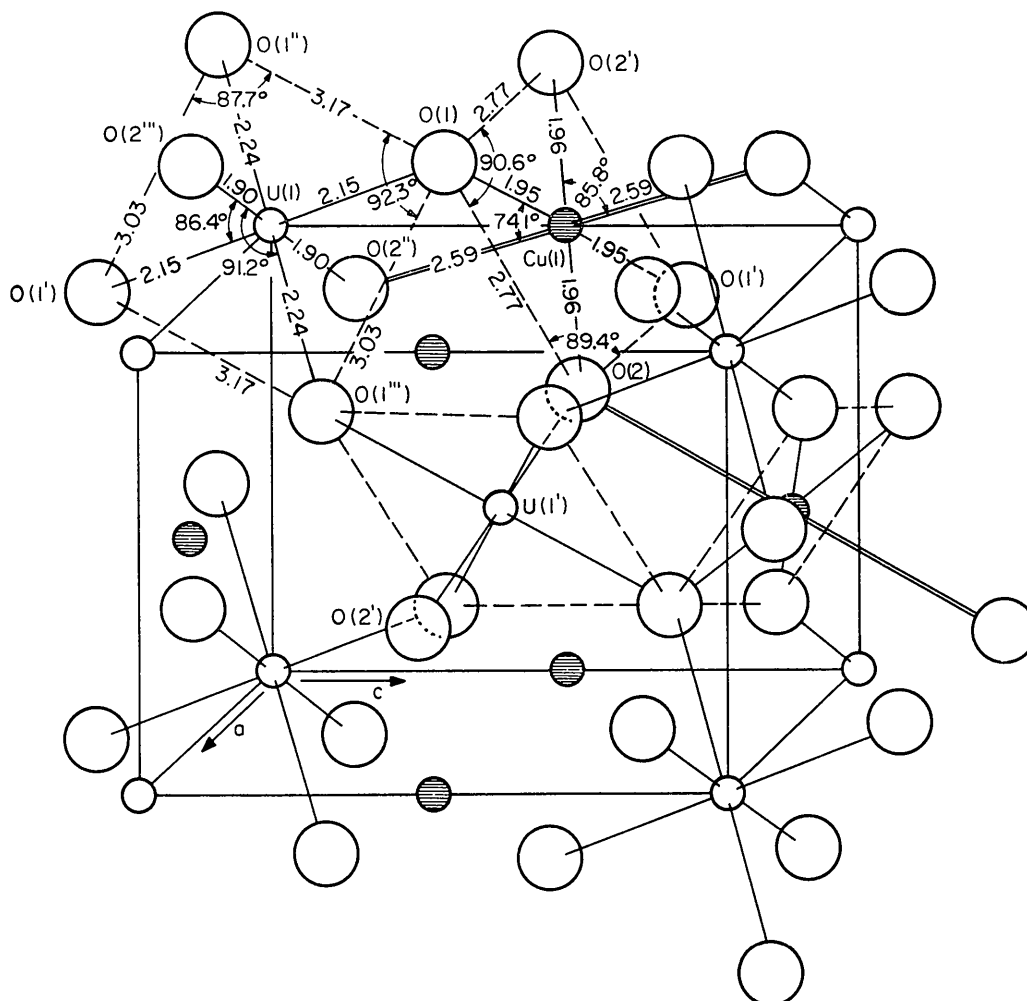


Fig. 1. Perspective view of $CuUO_4$ structure.

Table 3. *Interatomic distances and bond angles*

Within U-O configuration	
U(1)—O(1)	2.15 ± 0.02 Å
U(1)—O(1')	2.15 ± 0.02
U(1)—O(1'')	2.24 ± 0.02
U(1)—O(1''')	2.24 ± 0.02
U(1)—O(2'')	1.90 ± 0.02
U(1)—O(2''')	1.90 ± 0.02
O(1)—O(1'')	3.17 ± 0.02
O(1')—O(1''')	3.17 ± 0.02
O(1)—O(1''')	3.03 ± 0.02
O(1')—O(1'')	3.03 ± 0.02
O(2''')—O(1)	2.96 ± 0.03
O(2''')—O(1')	2.78 ± 0.03
O(2''')—O(1'')	2.92 ± 0.03
O(2''')—O(1''')	2.99 ± 0.03
<O(2''')—U(1)—O(1')	86.4 ± 0.6°
<O(2''')—U(1)—O(1''')	91.2 ± 0.6
<O(1')—O(1'')—O(1)	87.7 ± 0.7
<O(1'')—O(1)—O(1''')	92.3 ± 0.7
Within Cu-O configuration	
Cu(1)—O(1)	1.95 ± 0.02 Å
Cu(1)—O(1')	1.95 ± 0.02
Cu(1)—O(2)	1.96 ± 0.02
Cu(1)—O(2')	1.96 ± 0.02
Cu(1)—O(2'')	2.59 ± 0.02
Cu(1)—O(2''')	2.59 ± 0.02
O(2)—O(1')	2.77 ± 0.03
O(1')—O(2')	2.77 ± 0.03
O(2')—O(1)	2.77 ± 0.03
O(1)—O(2)	2.77 ± 0.02
<O(2')—O(1)—O(2)	90.6 ± 0.6°
<O(1)—O(2)—O(1')	89.4 ± 0.6
<O(2'')—Cu(1)—O(1)	74.1 ± 0.6
<O(2''')—Cu(1)—O(2')	85.8 ± 0.5
Metal-metal	
U(1)—Cu(1)	3.284 ± 0.003
U(1)—Cu(1')	3.693 ± 0.004
U(1)—U(1')	3.969 ± 0.004
Cu(1)—Cu(1')	3.969 ± 0.004

bonds about the copper atom are 2.77 Å each. Here too, the configuration is nearly square, with included angles of 89.4° and 90.6°. Two additional oxygen atoms, derived from uranyl oxygens, form copper-oxygen bonds at long distances on either side of the

Cu-4(0) plane. The bonds Cu(1)—O(2'') and Cu(1)—O(2''') each of length 2.59 Å are collinear but are not quite normal to the square planar copper-oxygen array. In the figure, these bonds, shown as double lines, make angles of 74.1° and 85.8° with the primary copper-oxygen bonds.

The bond strengths for the six oxygen bonds about a uranium atom are made up as follows: 1.90 Å (1.35), 2.15 Å (0.88), and 2.24 Å (0.73). The total bond strength is thus 5.92 which, of course, is 6 within our experimental error. These are based on the bond strength data of Zachariasen & Plettinger (1959) for U^{VI}.

The oxygen array surrounding the copper atoms is formed of two uranyl and two secondary oxygen atoms. Each uranyl oxygen atom is bonded to one uranium atom at a distance of 1.90 Å, a copper atom at 1.96 Å, and a second copper atom at 2.59 Å. The bond strength corresponding to the U—O distance of 1.90 Å is 1.35; the remainder of 0.65 is the fractional valence in the Cu—O bond for bonding. On the other hand, each secondary oxygen atom forms bonds of 2.15 Å and 2.24 Å with a uranium atom and one at 1.95 Å with a copper atom. This leaves a bond strength contribution of 0.39 for the copper atom. Hence, the total bond strength assignable to the copper atom is $2 \times 0.65 + 2 \times 0.39 = 2.1$. Thus, all bond distances are quite consistent with available bond strength data. It is not possible, however, to determine bond strength values for the very long Cu—O bonds.

References

- BRISI, C. (1963). *Annali di Chimica*, **53**, 325.
 CROMER, D. T. (1965). *Acta Cryst.* **18**, 17.
 HOEKSTRA, H. R. & MARSHALL, R. H. (1967). *Some Uranium-Transition Metal Double Oxides. Advances in Chemistry Series No. 71*, 211. Washington: American Chemical Society.
International Tables for X-ray Crystallography. (1962) Vol. III. Birmingham: Kynoch Press.
 TOKONAMI, M. (1965). *Acta Cryst.* **19**, 486.
 ZACHARIASEN, W. H. & PLETTINGER, H. A. (1959). *Acta Cryst.* **12**, 526.