JOURNAL OF SOLID STATE CHEMISTRY **41,** 286–292 (1982)

Structure of the Copper(I) Tantalum Oxide, $Cu_5Ta_{11}O_{30}$

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Received August 20, 1981; in final form October 27, 1981

The structure of hexagonal $Cu_5Ta_{11}O_{30}$ (space group $P\bar{6}2c$) has been determined from single-crystal diffractometer data. The cell dimensions are $a = 6.2297(2)$ Å and $c = 32.550(2)$ Å, and the cell content is two formula units. The structure is related to those of $CaTa_4O_{11}$ and $CeTa_7O_{19}$ and contains alternately single and double layers of TaO_7 pentagonal bipyramids sharing edges in the equatorial plane in the same way as UO_7 in α-U_3O_8. The layers are connected by TaO_6 octahedra and linear CuO_2 groups, both formed by the apex oxygens of the TaO_7 bipyramids. Refinement was made with the least-squares technique using 729 reflections, of which 422 were independent. The conventional R value was 3.9%.

Introduction

Studies of the system Cu_2O–Ta_2O_5 at temperatures from 800 to 1100°C (*1*) showed the existence of two hexagonal phases with probable compositions $Cu_5Ta_{11}O_{30}$ and $Cu_3Ta_7O_{19}$. Both are structurally related to earlier reported double oxides of niobium or tantalum with sodium, calcium (*2*), yttrium (*3*), and cerium (*4*), among others. They all contain layers of pentagonal bipyramids of oxygen around niobium (tantalum) which determine the length, 6.2 Å, of the a axis. The layers are interleaved by octahedral sites, which are occupied by Nb or Ta atoms, and also by sites of 7- or 8-coordination, which contain the other metal species. The Cu(I) atom, however, is not likely to occupy the same site types, and the new copper compounds were thus considered interesting objects of study. The structure of $Cu_5Ta_{11}O_{30}$ has therefore been determined and is described in this article. A summary of the various compounds of this structural family was given recently (*5*).

Experimental

A yellow fine-crystalline phase was obtained from a mixture of Cu_2O (Matheson, Coleman & Bell, min 96%) and Ta_2O_5 (Fluka AG, Buchs SG, min 99.9%), or of Cu (Kebo, min 99.9%), CuO (Baker Analyzed, min 99.9%), and Ta_2O_5, with weighed-in composition $Cu_2O \cdot 2.2Ta_2O_5$, when heated at 1000°C in an evacuated silica tube. ($Cu_2O \cdot 2.1\ Ta_2O_5$ contained some Cu_2O visible in a microscope, while $Cu_2O \cdot 2.2Ta_2O_5$ showed only very weak lines of Ta_2O_5 in the powder pattern.)

The Guinier powder pattern was registered with monochromatized Cu$K\alpha_1$ radiation and with potassium chloride as an internal standard. The film, which was measured and evaluated with a film scanner

0022-4596/82/030286-07$02.00/0

system (*6*), could be indexed hexagonally with the cell dimensions given in Table I. The unit cell parameters were refined with the program PIRUM (*8*).

Crystals large enough for single-crystal data collection were obtained in a sample heated at 1100°C for 5 days. Weissenberg films showed the Laue symmetry $6/mmm$ and hhl reflections to be present only with $l = 2n$. Intensity data were collected on a Siemens AED diffractometer, using graphite-monochromatized Cu$K\alpha$ radiation, with the 5-values technique. The diameter of the irregular crystal used was roughly 0.04–0.07 mm. The crystal was mounted with the a^* axis parallel to the instrument's ϕ axis, and reflections were registered within the sector with positive h, k, and l out to $\theta = 70°$, and with positive h and negative k and l to $\theta = 30°$. Some of the reflections between 60 and 70° were excluded due to high background given by the goniometer head in some positions. The data were corrected for absorption and the L-p factor. The linear absorption coefficient for Cu$K\alpha$ radiation was unfavorably high, 982 cm^{-1}, but due to the long c axis Mo radiation could not be used. This fact, together with the difficulty in determining the shape of the crystal, made the absorption correction rather uncertain and probably introduced a systematic error. Reflections hkl and khl did not differ significantly, and no hhl reflections with $I/\sigma(I) \geq 3$ were observed for $l = 2n + 1$.

TABLE I

CRYSTALLOGRAPHIC DATA FOR $Cu_5Ta_{11}O_{30}$. UNIT CELL a = 6.2297(2) Å, c = 32.550(2) Å, V = 1094.0 $Å^3$. SPACE GROUP $P\bar{6}2c$; UNIT CELL CONTENT Z = 2; DENSITY OBSERVED 8.39 g cm^{-3}, CALCULATED 8.46 g cm^{-3}

d_{obs} (Å)	I	hkl	$2\theta_{obs}$ (°)	$\Delta 2\theta \times 10^{3\,a}$ (°)
8.12	181	0 0 4	10.881	18
5.418	1055	0 0 6	16.346	20
5.389	138	1 0 0	16.435	18
5.318	584	1 0 1	16.657	14
5.121	279	1 0 2	17.304	2
4.825	369	1 0 3	18.374	23
4.066	223	0 0 8	21.844	18
3.825	65	1 0 6	23.237	4
3.521	104	1 0 7	25.276	11
3.254	2572	0 0 10	27.389	11
3.116	871	1 1 0	28.624	−11
3.060	3881	1 1 2	29.160	−7
3.002	138	1 0 9	29.731	16
2.909	1061	1 1 4	30.710	0
2.786	36	1 0 10	32.100	11
2.701	1557	1 1 6 2 0 0	33.144	7 −40
2.689	34	2 0 1	33.297	−4
2.619	841	2 0 3	34.214	−11
2.594	41	1 0 11	34.543	0
2.560	191	2 0 4	35.019	3
2.474	2120	1 1 8	36.289	−4
2.4160	212	2 0 6	37.184	−10
2.3330	674	2 0 7	38.560	7
2.2707	27	1 0 13	39.660	8
2.2508	382	1 1 10	40.025	−7
2.1621	171	2 0 9	41.743	4
2.0769	155	2 0 10	43.541	2
2.0452	740	1 1 12	44.250	8
2.0344	852	2 1 1 0 0 16	44.499	18 0
2.0040	57	2 1 3	45.211	2

Note. 86 observed lines are indexed. F_{30} = 57 (0.0088, 60) (*7*), F_{86} = 51 (0.0085, 200).

[a] $\Delta 2\theta = 2\theta_{obs} - 2\theta_{calc}$.

Structure Determination

The c axis of $CaTa_4O_{11}$ (*2*), containing single layers of pentagonal bipyramids, is 12.3 Å. The c axes of YTa_7O_{19} (*3*) and $CeTa_7O_{19}$ (*4*) with double layers of pentagonal bipyramids are about 20 Å. The length of the c axis of $Cu_5Ta_{11}O_{30}$ is approximately the sum of the above values, and the composition with respect to tantalum and oxygen is likewise the sum of the compositions of the single- and double-layer structures. Thus the structure was assumed to have a tantalum–oxygen network with both single and double layers of pentagonal bipyramids held together by octahedrally coordinated tantalum atoms.

TABLE II

POSITIONAL AND THERMAL PARAMETERS WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	Position	x	y	z	$U_{11} \times 10^3$ [a]	$U_{22} \times 10^3$	$U_{33} \times 10^3$	$U_{12} \times 10^3$	$U_{13} \times 10^3$	$U_{23} \times 10^3$
Ta(1)	6*g*	0.3629(2)	0	0	2.7(5)	1.4(6)	5.1(6)	0.7(3)	0.2(2)	0.4(4)
Ta(2)	12*i*	0.6683(2)	0.9723(2)	0.19200(3)	0.6(5)	3.7(5)	4.1(5)	0.0(4)	0.2(3)	−0.5(3)
Ta(3)	4*f*	$\frac{1}{3}$	$\frac{2}{3}$	0.09705(5)	11.3(6)	11.3(6)	1.4(6)	5.7(3)	0	0
Cu	12*i*[b]	0.3333(8)	0.1635(8)	0.0952(1)	26(3)	16(2)	14(2)	14(2)	−3(2)	−7(2)
O(1)	6*g*	0.748(3)	0	0	6(4)					
O(2)	4*f*	$\frac{1}{3}$	$\frac{2}{3}$	0.9904(6)	1(4)					
O(3)	12*i*	0.371(2)	0.938(2)	0.0591(3)	1(2)					
O(4)	12*i*	0.417(3)	0.086(3)	0.1906(4)	15(3)					
O(5)	4*f*	$\frac{1}{3}$	$\frac{2}{3}$	0.1969(7)	13(5)					
O(6)	4*e*	0	0	0.1818(7)	14(5)					
O(7)	6*h*	0.693(3)	0.962(3)	$\frac{1}{4}$	3(3)					
O(8)	12*i*	0.604(2)	0.906(3)	0.1296(4)	4(3)					

[a] Anisotropic temperature factors are given in the form $\exp\{-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2hlb^*c^*U_{23})\}$.

[b] An occupancy factor 0.8333 (= $\frac{5}{6}$) was used.

The Laue symmetry and the absences gave the space group alternatives $P6_3mc$, $P\bar{6}2c$, and $P6_3/mmc$. $P\bar{6}2c$ was chosen on the basis of the structural arguments given above. After a few trials acceptable tantalum positions were obtained, and then copper positions were derived from a difference synthesis with only the tantalum positions included. The oxygen positions could also be seen in difference syntheses.

Since the strong reflections showed systematically too low F_{obs} values in the least-squares refinement, an isotropic correction factor for secondary extinction (*9*) was included. In the final refinement with a full matrix least-squares program 729 reflections with $I > 2\sigma(I)$ from the positive sector (of which 422 were independent) were included. Due to the systematic errors from the absorption correction, this way of averaging the data gave somewhat better values of the oxygen temperature factors than a refinement with a unique set of data. The differences were not significant, however. A modified $\sigma(F)$ was used in the weight function, viz., $\sigma(F)_{mod} = (\sigma(F)^2 + (0.011|F|)^2)^{1/2}$. Scattering factors for Ta^0, Cu^0, and O^0 were used in the calculations (*10*).

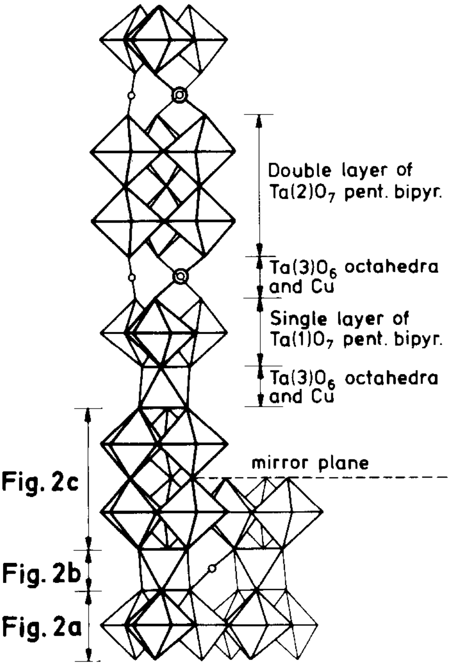

FIG. 1. Part of the structure viewed along the *a* axis, showing the sequence of polyhedra along the *c* axis. The shifts of some oxygens out of the equatorial planes have been ignored.

TABLE III

INTERATOMIC DISTANCES (Å)

Ta(1) pentagonal bipyramid		O(42)	–O(6)	2.40(2)
Ta(1)–O(11)	2.402(18)		–O(7)	2.79(2)
–O(12)	2.006(4)		–O(81)	3.10(2)
–O(21)	2.015(3)		–O(81)	3.10(2)
–O(31)	1.967(10)	O(43)	–O(7)	2.99(2)
O(11)–O(21)	2.39(2)		–O(81)	3.00(2)
–O(31)	2.91(2)	O(5)	–O(7)	2.70(2)
O(12)–O(13)	2.72(4)		–O(81)	2.71(3)
–O(31)	2.78(1)	O(6)	–O(7)	2.86(2)
O(13)–O(31)	3.08(2)		–O(81)	2.80(2)
O(21)–O(31)	2.74(2)			
O(22)–O(31)	2.74(2)	Ta(3) octahedron		
		Ta(3)	–O(31)	2.012(10)
Ta(2) pentagonal bipyramid			–O(81)	1.918(11)
Ta(2)–O(41)	2.012(16)	O(31)	–O(32)	2.75(2)
–O(42)	1.983(16)		–O(81)	2.78(2)
–O(43)	2.427(16)		–O(82)	2.81(2)
–O(5)	2.008(2)	O(81)	–O(82)	2.77(2)
–O(6)	2.013(4)			
–O(7)	1.898(2)	Cu coordination		
–O(81)	2.071(11)	Cu	–O(31')	1.933(11)
O(41)–O(42)	2.68(3)		–O(83)	1.915(12)
–O(5)	2.40(2)	∠O(31')–Cu–O(83)		177.9(5)°
–O(7)	2.94(2)			
–O(7)	2.94(2)			
–O(81)	2.80(2)			

Note. The oxygen numbers refer to Fig. 2. Only one of each set of symmetry-related distances is given.

The final positional and thermal parameters are shown in Table II. The low values of some oxygen temperature factors and of U_{33} for Ta(3) are probably due to the errors in the absorption correction. The conventional *R* value was 3.9%. A difference Fourier map showed a maximum electron density of 0.14 e $Å^{-3}$. The interatomic distances are given in Table III.[1]

Description and Discussion of the Structure

The structure contains layers of pentago-

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[1] The table of F_o and F_c is available at the Secretariat of this Institute.

nal bipyramids interleaved by octahedral Ta sites and Cu positions. The layers of polyhedra form the sequence along the *c* axis that is shown in Fig. 1. Each type of layer is projected along the *c* axis in Fig. 2.

Figure 2a shows a single layer of $\mathrm{Ta(1)O_7}$ bipyramids. The Ta(1)–O(11) distance is larger than the other Ta(1)–O distances (see Table III). This lengthening is a consequence of the distortion of the $\mathrm{Ta(1)O_5}$ pentagons necessary to make possible their mutual linking by common edges. This layer of polyhedra is of a type found in α-$\mathrm{U_3O_8}$ (*11*), where pentagonal bipyramid layers are stacked, sharing apex oxygens.

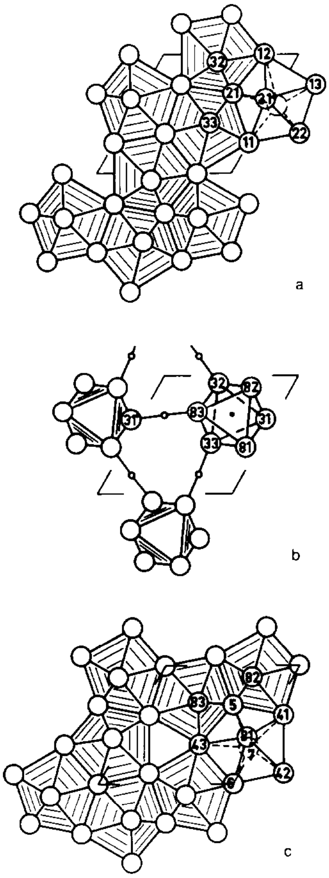

FIG. 2. Projections along the *c* axis of (a) the single layer of $\mathrm{Ta(1)O_7}$ pentagonal bipyramids, (b) the layer of $\mathrm{Ta(3)O_6}$ octahedra and linear $\mathrm{CuO_2}$, and (c) the double layer of $\mathrm{Ta(2)O_7}$ pentagonal bipyramids. ●, Ta; o, Cu; ○, O. The first digit in the oxygen numbering is the number in Table II. There is a mirror plane through O(7) in (c); thus the O(8) apex oxygens recur as the bottom of the lower layer. Hence, O(81), O(82), and O(83) in (b) are related by the mirror plane to identically numbered atoms in (c).

Figure 2b shows the $\mathrm{Ta(3)O_6}$ octahedra and the copper positions. Two successive pentagonal bipyramid layers have such relative positions (Fig. 2a,c) that three apex oxygens from each layer form the octahedral sites for the tantalum atoms. The three oxygens from one layer are shifted toward each other to give the octahedron a proper size (see, e.g., O(31), O(32), and O(33) in Fig. 2a). This evidently affects the position of the O(21) atom, which is squeezed out of the $z = 0$ plane, thus adjusting the O–O distances. The copper atoms are situated between two apex oxygens of adjacent layers to give a linear 2-coordination normal for Cu(I). Though the significance is doubtful, the thermal ellipsoid of Cu has the expected shape, with the shortest principal axis roughly parallel to the bonding direction.

Figure 2c shows a double layer of $\mathrm{Ta(2)O_7}$ bipyramids. The structure has a mirror plane through the common apex oxygens. This layer is rotated and translated relative to the single layer so that O(81), O(82), and O(83), together with O(31), O(32), and O(33), give the Ta(3) atoms their octahedral environment. In other respects the layers are very similar.

The Cu–O bond distances (~1.92 Å) are a little longer than those of some earlier reported Cu(I) compounds. In, e.g., $\mathrm{Cu_2O}$ the Cu–O distance is 1.849 Å (*12*), and in $\mathrm{CuFeO_2}$ 1.835 Å (*13*). In $\mathrm{CuNbO_3}$, however, the Cu–O distances vary between 1.82 and 2.00 Å, with a mean value of 1.91 Å (*14*). In the present structure the next Cu–O distance after those given in Table III is 2.75 Å, and the Cu–Cu distances are 3.115 Å. The Ta–O and O–O distances are throughout in close agreement with values found for similar substances, such as $CaTa_4O_{11}$ (*2*).

The structures of $Na_2Nb_4O_{11}$ and $CaTa_4O_{11}$ (*2*) only contain single pentagonal bipyramid layers alternating with layers of polyhedra formed by the apex oxygens: small, rather regular octahedra around niobium (tantalum), and larger, irregular polyhedra containing sodium or calcium (Fig. 3). As in $Cu_5Ta_{11}O_{30}$, the O atoms corresponding to position O(2) lie a little out of the equatorial plane (cf. Fig. 2a). This shift in $Na_2Nb_4O_{11}$ and $CaTa_4O_{11}$ brings the oxygen closer to Na and Ca, causing Na to be 7-coordinated and Ca to be 8-coordinated, while in the copper compound the copper coordination is not affected by this shift.

It should be observed that the copper positions in $Cu_5Ta_{11}O_{30}$ correspond to sites on the edges of the polyhedra surrounding the Na atoms of $Na_2Nb_4O_{11}$. This allows a linear coordination for copper between the apex oxygens and gives room for three copper, instead of two sodium, atoms. Thus, the ideal composition would be $Cu_6Me_{11}O_{30}$. Since the stoichiometry only allows five Cu, the copper position is not fully occupied. Refinement of the occupancy parameter gave the value 0.79(2), slightly lower than $\frac{5}{6}$ though scarcely significantly so. There were, however, no indications of mixed oxidation numbers. The yellow color agrees with that of several Cu(I) double oxides prepared at this Institute (*15, 16*), which are yellow or red, like many other compounds with charge-transfer transitions. The presence of both Cu(I) and Cu(II) would most probably give a black sample. Nor has any homogeneity range been observed. Therefore the final refinement was made with a fixed value of $\frac{5}{6}$ for the occupancy parameter.

The structure of $CeTa_7O_{19}$ (*4*) consists of only double layers of pentagonal bipyramids, separated by 6-coordinated Ta and 8-coordinated Ce, though with some disorder (*17*). The $Cu_3Ta_7O_{19}$ phase is also of the double-layer type (*5*). If the copper sites are of the same type as in $Cu_5Ta_{11}O_{30}$, they will be fully occupied, according to the stoichiometry.

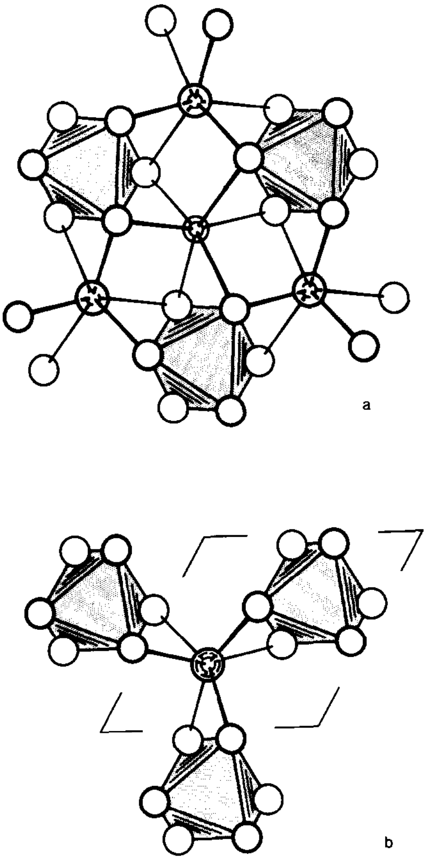

FIG. 3. (a) Layer of NbO_6 octahedra (illustrated as solid polyhedra) and 7-coordinated Na atoms (bonds to oxygens shown) in $Na_2Nb_4O_{11}$, projected perpendicular to the *ab* plane of the *C* centered monoclinic cell. (b) Layer of TaO_6 octahedra and 8-coordinated Ca atoms in $CaTa_4O_{11}$, projected along the hexagonal *c* axis. There are oxygens above *or* below Na, and above *and* below Ca; these oxygens lie in the equatorial planes of the pentagonal bipyramids. Corresponding oxygens are not included in Fig. 2b since they do not belong to the Cu coordination.

Acknowledgments

I sincerely thank Professor Arne Magnéli for his encouraging interest and valuable discussions and comments on the manuscript. This work has been carried out within a research program supported by the Swedish Natural Science Research Council.

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