6. Campbell, H. A., Mashburn, L. T., Boyse, E. A. and Old, L. J. *Biochemistry* **6** (1967) 721.
7. Gale, E. F. *Methods Biochem. Analy.* **4** (1957) 255.
8. Eriksson, C. and von Sydow, E. *J. Food Sci.* **29** (1964) 58.

Received November 1, 1967.

On the Crystal Structure of Copper Wolframate

ELIZABETH GEBERT* and LARS KIHLBORG

Institute of Inorganic and Physical Chemistry, University of Stockholm, Stockholm Va, Sweden

Investigations have been started at this Institute on phases occurring in the Cu—Mo—O and Cu—W—O systems in order to elucidate their crystal structures and electric and magnetic properties. Some results of studies on the copper-wolfram-oxygen system obtained so far are reported below.

Samples were prepared by mixing CuO, Cu_2O, WO_3, and WO_2 in various proportions and heating them in evacuated, sealed platinum tubes at about 800°C for a period of several days. Powder patterns taken of the preparations indicated the formation of two intermediate phases, Cu_3WO_6 and a second which we will here designate $CuWO_{4-x}$ (see below). The former is a previously unknown phase with a cubic structure which will be reported elsewhere.[1] The latter appears to be identical with the phase reported as $Cu_{0.77}WO_3$ by Conroy and Sienko [2] and later as $Cu_xWO_{3+\delta}$ by Sienko and Weller.[3]

Preparations made with starting compositions around $CuWO_4$ gave powder patterns of the type listed in Table 1. The bulk of these samples consisted of dark yellow brown, polyhedric crystals which were more or less transparent but which all seemed to be twinned. With the aid of precession and Weissenberg photographs the powder pattern could be indexed on the basis of the triclinic unit cell parameters given in Table 2. By the transformation (0,1,0/−1,0,−1/0,0,1) an alternative cell is obtained which is in close agreement with that reported for "$Cu_{0.77}WO_3$".[2]

Table 1. X-Ray powder diffraction data for $CuWO_{4-x}$, $CuK\alpha_1$ radiation ($\lambda = 1.54051$ Å) $\Delta = (\sin^2\theta_{obs} - \sin^2\theta_{calc})$.

I	d_{obs} Å	$\sin^2\theta_{obs} \times 10^5$	$h\,k\,l$	$\Delta \times 10^5$
m	5.799	1764	0 1 0	− 5
s	4.662	2730	1 0 0	0
w	3.876	3949	1 1 0	− 4
mw	3.771	4171	0 $\bar{1}$ 1	4
m	3.684	4371	0 1 $\bar{1}$	2
ms	3.433	5033	1 $\bar{1}$ 0	−12
			1 0 $\bar{1}$	12
ft	3.304	5435	1 0 1	− 1
s	3.113	6124	1 1 $\bar{1}$	−19
m	2.962	6760	1 1 1	− 1
w	2.895	7081	0 2 0	5
m	2.824	7438	1 $\bar{1}$ $\bar{1}$	1
m	2.7848	7650	1 $\bar{1}$ 1	0
w	2.6094	8713	1 2 0	− 1
mw	2.5159	9373	0 $\bar{2}$ 1	1
m	2.4632	9778	0 2 $\bar{1}$	1
s	2.4359	9999	0 0 2	3
m	2.3311	10918	2 0 0	− 2
w	2.2593	11623	1 2 1	0
mw	2.1954	12309	1 0 $\bar{2}$	− 2
ft	2.1373	12988	2 0 $\bar{1}$	−15
w	2.1239	13152	1 0 2	11
mw	2.1100	13326	1 1 $\bar{2}$	− 5
mw	2.1036	13407	1 $\bar{2}$ 1	6
			1 $\bar{2}$ $\bar{1}$	16
w	2.0903	13578	2 1 $\bar{1}$	− 2
w	2.0743	13789	2 $\bar{1}$ 0	9
mw	2.0176	14575	1 1 2	8
mw	2.0148	14615	2 1 1	2
w	1.9997	14837	1 $\bar{1}$ $\bar{2}$	9
m	1.9731	15239	1 $\bar{1}$ 2	−14

Weissenberg data were collected from a twinned crystal using Mo$K\alpha$ radiation. Positions for the metal atoms were derived from a three-dimensional Patterson synthesis assuming space group $P\bar{1}$. Probable oxygen positions were located in a difference synthesis. The subsequent least-squares refinement gave an R-value of 0.20 which was considered reasonable in view of the inherently poor data obtainable from this twinned crystal. The resulting B-values and interatomic distances indicate

* On leave from Argonne National Laboratory, Argonne, Illinois, USA.

Table 2. Preliminary atomic parameters for $CuWO_{4-x}$. The atomic distribution given below does not reflect the possible deviation from the ideal ABO_4 stoichiometry.

$a = 4.7026(\pm 6)$ Å, $b = 5.8389(\pm 7)$ Å, $c = 4.8784(\pm 6)$ Å
$\alpha = 91.677\ (\pm 9)°$, $\beta = 92.469\ (\pm 7)°$, $\gamma = 82.805\ (\pm 10)°$.
Space group $P\bar{1}$.

Atom	Position	x	y	z	B
W	2 *i*	0.0207(± 4)	0.1743(± 3)	0.2545(± 4)	−0.06(± 4)
Cu	2 *i*	0.4909(± 15)	0.6580(± 10)	0.2443(± 15)	0.25(± 9)
O(1)	2 *i*	0.265(± 10)	0.370(± 7)	0.416(± 10)	0.6(± 6)
O(2)	2 *i*	0.207(± 10)	0.876(± 7)	0.443(± 10)	0.5(± 5)
O(3)	2 *i*	0.721(± 9)	0.385(± 6)	0.114(± 9)	0.2(± 4)
O(4)	2 *i*	0.788(± 8)	0.898(± 5)	0.062(± 9)	0.0(± 4)

that the structure is essentially correct. Preliminary structure parameters are given in Table 2.

The structure is a distorted version of the wolframite type. The structures of $NiWO_4$[4] and $CdWO_4$[5] which are of this monoclinic type have been determined in recent years. The distortion in $CuWO_{4-x}$ is mainly reflected in the deviation of γ from 90°. The wolfram atoms are octahedrally coordinated by six oxygens at distances ranging from 1.83 to 2.22 Å. The copper atoms are bonded to four oxygens approximately in a plane at distances 1.92−2.00 Å, with two additional oxygen atoms at 2.30 and 2.32 Å completing a distorted octahedron.

Late in this structure investigation a single crystal was found from which diffractometer data are now being collected. We hope these will give more detailed information about the structure.

Although the studies reported above have proved that the structure is of an ABO_4 type, the stoichiometry of the phase needs some further comments.

The B-values obtained by refinement are rather sensitive to incorrect assumptions about the scattering factors. The values obtained for the metal atoms in the present case are reasonable, considering the lack of absorption correction, and do not indicate any extensive substitution or subtraction on the cation positions. We therefore believe that the Cu/W ratio is close to unity, which is also supported by the phase analysis. It is not possible, however, to decide from the powder patterns of the preparations made hitherto, whether the phase is oxygen deficient and whether it has an extended homogeneity range.

The density of the phase was determined by a pycnometric method on three different samples. The values obtained agreed very well and gave an average of $\varrho_{obs} = 7.44\ (\pm 7)$ g/cm³. This should be compared with the following densities calculated for two units of the indicated formula per cell: $CuWO_4$ 7.73, $CuWO_{3.5}$ 7.53, $CuWO_3$ 7.34, $Cu_{0.77}WO_3$ 6.98 g/cm³. The density measurements thus suggest a considerable oxygen deficiency, which, on the other hand, seems contradictory to the fact that the crystals are more or less transparent.

The stoichiometry of copper wolframate evidently needs further studies which are now being made at this institute. Also high pressure techniques are being used for this purpose. Until further results have been obtained we prefer the general formula $CuWO_{4-x}$, used above, for this phase.

Acknowledgements. The work reported here has been financially supported by the *Swedish Natural Science Research Council*. Funds for the use of computers were made available by the *Computer Division* of the *National Swedish Rationalization Agency*. One of us (E.G.) expresses appreciation for a grant received from the *American-Scandinavian Foundation*.

1. Gebert, E. and Kihlborg, L. *Acta Chem. Scand. In press.*
2. Conroy, L. E. and Sienko, M. J. *J. Am. Chem. Soc.* **79** (1957) 4048.
3. Sienko, M. J. and Weller, P. F. *Inorg. Chem.* **1** (1962) 324.
4. Keeling, Jr., R.O. *Acta Cryst.* **10** (1957) 209.
5. Chichagov, A. P., Ilyukhin, V. V. and Belov, N. V. *Dokl. Akad. Nauk. SSSR* **166** (1966) 87.

Received November 3, 1967.