ACTA CHEMICA SCANDINAVICA 7 (1953) 315–324

Studies on the Hexagonal Tungsten Bronzes of Potassium, Rubidium and Cesium

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Opinions have diverged concerning the chemical character of the product obtained in the form of a dark blue powder or sometimes as hexagonal flaky crystals when mixtures of potassium tungstate and tungsten trioxide rich in the latter are reduced. Thus von Knorre [1] considered it to be potassium octatungstate, $K_2O \cdot 8WO_3$, while Brunner [2] assumed that it consists of a mixture of tungsten bronzes, $K_2W_5O_{15}$, $K_2W_6O_{18}$, and $K_2W_8O_{24}$. Schäfer [3], who synthetized a corresponding rubidium preparation, described this substance as an octatungstate.

In a recent communication from this institute [4] on the preparation and composition of the alkali tungsten bronzes results were given of careful analyses of these blue potassium and rubidium preparations as well as of the corresponding cesium product previously unknown. The compositions of these three substances were found to be in excellent agreement with the general formula Me_xWO_3 common to all hitherto known tungsten bronzes and the idea of von Knorre and Schäfer could thus be definitely excluded. Moreover, X-ray powder analysis showed that each of the three products contained only one phase, these three tungsten bronzes being hexagonal and isomorphous. Unit cell dimensions derived from powder photographs of various preparations, obtained by slight modifications of the experimental conditions mentioned in reference no. 4, are listed in Table 1. (For discussion of the relation between composition and unit cell dimensions *v. infra.*) The observed density values indicate that the elementary cell contains six formula units of Me_xWO_3.

Table 2 gives part of the powder pattern of the rubidium bronze preparation $Rb_{0.29}WO_3$, the other samples only showing minor alterations of the positions and intensities of the reflections. No attempts have been made to find the extension of the homogeneity ranges of the phases.

Table 1. Unit cell dimensions, density and electrical conductivity of hexagonal alkali tungsten bronzes.

Composition	a Å *	c Å	V Å^3	ϱ_{obs}	ϱ_{calc} **	$\varkappa$ ohm^{-1} cm^{-1}
$K_{0.27}WO_3$	7.40	7.56	358			
$K_{0.31}WO_3$	7.37	7.54	354	6.6	6.86	20
$Rb_{0.27}WO_3$	7.39	7.54	357			
$Rb_{0.29}WO_3$	7.38	7.56	357	7.4	7.16	35
$Cs_{0.30}WO_3$	7.38	7.59	358	7.5	7.56	15
$Cs_{0.32}WO_3$	7.42	7.63	363			

* The unit cell dimensions are expressed in true Å units. Probable error $\pm$ 0.01 Å.

** Calculated on the basis of a cell content of six formula units of Me_xWO_3.

Quite recently Brimm and co-workers [5] reported the preparation of a blue sodium potassium tungsten bronze of composition $Na_{\sim 0.08}K_{0.13}WO_3$ giving the same X-ray powder pattern as the blue potassium compound obtained by heating appropriate mixtures of potassium tungstate, tungsten trioxide and tungsten at 1050° C in argon. The symmetry should be hexagonal and the unit cell dimensions $a = 7.44$ Å, $c = 22.80$ Å, the a axis thus being about the same and the c axis three times that of the bronzes described in this communication. No reflections indicating such a multiplication of the hexagonal axis have been observed in our X-ray photographs. It seems probable that the structure of the bronzes prepared by Brimm and co-workers corresponds to a superstructure of the lattice of the hexagonal bronze type described below.

CRYSTAL STRUCTURE

The structure determination was carried out on the basis of single crystal photographs of a minute crystal chosen from the preparation $Rb_{0.27}WO_3$. This crystal was fairly elongated in the [10$\bar{1}$0] direction, which was used as the rotation axis. Rotation and Weissenberg photographs (layer lines 0—4) were taken with Cu-K radiation. The intensities were estimated visually and the correlation between the intensity scales of the layer lines was obtained from a "Weissenberg oscillation photograph" registering appropriate oscillation intervals of the various layer lines on the same film [6].

Table 2. Powder photograph of $Rb_{0,29}WO_3$, obtained in a Guinier focusing camera with Cu-Ka radiation. Comparison between observed (Weissenberg data) and calculated structure factor values.

	Powder data			Single crystal data	
h k i l	Intensity	$\sin^2\Theta_{obs}$	$\sin^2\Theta_{calc}$	$\lvert F_{obs}\rvert_{Wbg}$	F_{calc}
1 0 $\bar{1}$ 0	m	.0144	.0145	80	−110
0 0 0 2	st	.0415	.0415	580	−390
1 1 $\bar{2}$ 0	w	.0436	.0436	80	−110
1 1 $\bar{2}$ 1	v w	.0539	.0540	60	−60
1 0 $\bar{1}$ 2	st	.0558	.0560	240	180
2 0 $\bar{2}$ 0	v st	.0582	.0582	620	430
1 1 $\bar{2}$ 2	st	.0851	.0851	210	170
2 0 $\bar{2}$ 2	st	.0995	.0997	290	−250
2 1 $\bar{3}$ 1	w	.1120	.1122	—	60
3 0 $\bar{3}$ 0	w	.1308	.1309	130	−90
1 1 $\bar{2}$ 3	v w	.1369	.1371	80	60
2 1 $\bar{3}$ 2	m	.1433	.1433	80	100
0 0 0 4	m	.1658	.1662	520	440
3 0 $\bar{3}$ 2	w	.1722	.1724	90	150
2 2 $\bar{4}$ 0	st	.1746	.1746	310	390
1 0 $\bar{1}$ 4	v w	.1808	.1807	150	−80
3 1 $\bar{4}$ 0	w	.1891	.1891	100	−90
2 1 $\bar{3}$ 3	v w	.1950	.1953	—	−50
3 1 $\bar{4}$ 1	w	.1995	.1995	100	−110
1 1 $\bar{2}$ 4	v w	.2095	.2098	120	−80
2 2 $\bar{4}$ 2	st	.2162	.2161	150	−250
2 0 $\bar{2}$ 4	st	.2239	.2244	430	350
3 1 $\bar{4}$ 2	m	.2307	.2306	100	150
4 0 $\bar{4}$ 0	m	.2327	.2328	490	360
4 0 $\bar{4}$ 2	st	.2739	.2743	230	−230
3 2 $\bar{5}$ 0	v w	.2761	.2764	60	−60
3 1 $\bar{4}$ 3	w	.2823	.2826	80	100
3 2 $\bar{5}$ 1	v w	.2869	.2868	—	50
3 0 $\bar{3}$ 4	v w	.2975	.2971	80	−70
4 1 $\bar{5}$ 0	v w	.3056	.3055	80	−60
4 1 $\bar{5}$ 1	v w	.3157	.3159	100	90
3 2 $\bar{5}$ 2	m	.3177	.3179	80	110
2 2 $\bar{4}$ 4	st	.3405	.3408	170	320
4 1 $\bar{5}$ 2	w	.3470	.3470	100	110
3 1 $\bar{4}$ 4	w	.3554	.3553	80	−80
0 0 0 6	v w	.3740	.3739	370	−260
1 0 $\bar{1}$ 6	w	.3879	.3884	120	120

Table 2. cont.

$h\ k\ i\ l$	Powder data			Single crystal data	
	Intensity	$\sin^2\Theta_{obs}$	$\sin^2\Theta_{calc}$	$\lvert F_{obs}\rvert_{Wbg}$	F_{calc}
4 0 $\bar{4}$ 4	st	.3988	.3990	150	300
4 1 $\bar{5}$ 3			.3990	60	−80
3 3 $\bar{6}$ 1	v w	.4032	.4032	100	−130
4 2 $\bar{6}$ 0	m	.4074	.4073	260	250
1 1 $\bar{2}$ 6	v w	.4178	.4175	120	120
2 0 $\bar{2}$ 6	w	.4320	.4321	270	−220
3 3 $\bar{6}$ 2	v w	.4339	.4343	80	110
3 2 $\bar{5}$ 4	v w	.4431	.4426	—	−50
3 1 $\bar{4}$ 5	st	.4487	.4487	80	−90
4 2 $\bar{6}$ 2			.4488	180	−160
5 1 $\bar{6}$ 1	w	.4617	.4614	150	−120
4 1 $\bar{5}$ 4	v w	.4716	.4717	—	−50
2 1 $\bar{3}$ 6	w	.4760	.4757	80	100
3 3 $\bar{6}$ 3	v w	.4866	.4863	—	120
5 1 $\bar{6}$ 2	w	.4928	.4925	150	130

The Laue symmetry was found to be $6/mmm$ and the only reflections regularly missing were $hh\bar{2}hl$ with l odd, which is characteristic of the space-groups D^3_{6h}—$C6/mcm$, C^3_{6v}—$C6cm$, and D^3_{2h}—$C\bar{6}c2$. Furthermore the following regularities of the structure amplitudes could be observed:

1) Reflections $000l$. F^2 uniformly decreasing with l $(= 2n)$ increasing. (Reflections $000l$ absent when $l = 2n + 1$.)

2) Reflections $hkil$. F^2 generally low when l is odd.

These regularities imply that the tungsten atoms must be situated in (or very close to) planes extending normally to the hexagonal axis and $c/2$ apart and that the arrangement of these atoms must be approximately the same in neighbouring planes. In the Patterson function this corresponds to the sections $P(xy0)$ and $P(xy\frac{1}{2})$ containing all the heavy maxima and looking essentially the same.

The section $P(xy0)$ was only found to contain major maxima at the origin and at the centers of the sides and the area of the unit mesh. The height of the first was found to be somewhat less than twice that of the other ones, which among themselves were of equal magnitude. This appearance of the Patterson function is in accordance with the arrangement of six tungsten atoms in the point position $6(g)$ of the space-group $C6/mcm$ [7] (*cf.* Fig. 1a):

$x\ 0\ \frac{1}{4};\ 0\ x\ \frac{1}{4};\ \bar{x}\ \bar{x}\ \frac{1}{4};\ \bar{x}\ 0\ \frac{3}{4};\ 0\ \bar{x}\ \frac{3}{4};\ x\ x\ \frac{3}{4}$, with $x \approx 0.5$.

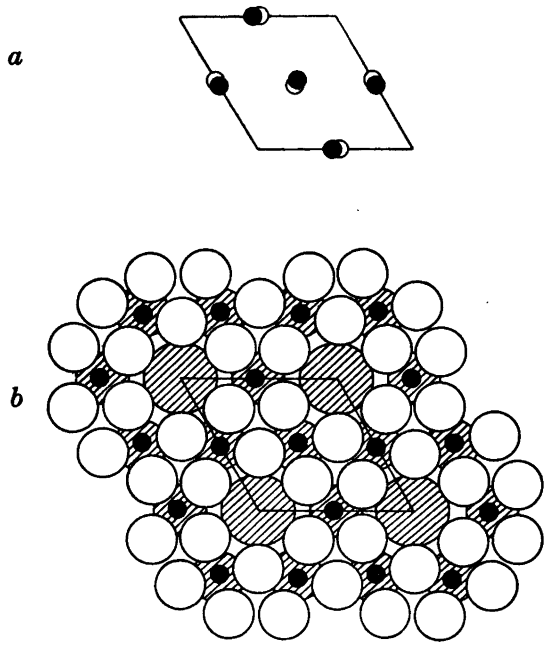

Fig. 1. The crystal structure of the hexagonal tungsten bronzes Me_xWO_3.

a) Positions of the tungsten atoms, the filled small circles representing atoms at $z = \frac{1}{4}$ *and the open ones atoms at* $z = \overline{\frac{1}{4}}$ $(\frac{3}{4})$.

b) Atomic arrangement of one layer of the structure, the circles of medium size corresponding to oxygen atoms at $z = 0$ *(marked with lines) and* $z = \frac{1}{4}$ *and the large ones to alkali atoms at* $z = 0$. *The atoms at* $z = \frac{1}{2}$ *are omitted to show the underlying atoms.*

It was found that a value of x equal to 0.48 gives fair agreement between the observed and calculated values of $F^2(hkil)$. Calculation of the section $\varrho(x0\frac{1}{4})$ of the electron density function gave support to this parameter value.

The interatomic distances corresponding to the positions of the tungsten atoms thus arrived at are 3.78 Å in the direction of the c axis and 3.70 Å parallel to the ab plane. Similar tungsten-tungsten distances have been found in several tungsten oxides and bronzes between the metal atoms of WO_6 octahedra joined by sharing corners [8]. Assuming an octahedral arrangement of the oxygen atoms around the tungsten atoms that should be present in the structure of the hexagonal bronzes a reasonable distribution of the eighteen oxygen atoms of the unit cell could be devised corresponding to the symmetry $C6/mcm$ with six atoms in the point position $6(f)$ and the remaining ones

in 12(*j*) ($x \approx 0.42$, $y \approx 0.22$) [7]. The corresponding tungsten-oxygen distances are 1.89—1.96 Å while the oxygen atoms are mutually 2.56—2.82 Å apart. Due to the relatively low X-ray scattering power of the oxygen atom this arrangement could not be verified by calculations of the electron density function.

This tungsten-oxygen lattice contains holes of considerable width (around the point position 2(*b*)), which were thought likely to accomodate the $6x$ (< 2) alkali atoms of the unit cell in a statistical distribution. This supposition could be verified by investigating the appearance of the electron density function along the line $0y0$, where a proper maximum was found to occur at $y = 0$. For the actual rubidium tungsten bronze these positions of the alkali atoms will lead to distances of 3.28 Å between the rubidium atom and the twelwe neighbouring oxygen atoms. The theoretical upper limit of x in the formula Me_xWO_3 will be 1/3.

The crystal structure thus derived may be summarized as follows (*cf.* Fig. 1 b)[7]:

Cell content: 6 Rb_xWO_3

Space group: D_{6h}^3—$C6/mcm$

$6x$	Rb	in	2(*b*)	: 000; $00\frac{1}{2}$.	
6	W	in	6(*g*)	: $x\ 0\ \frac{1}{4}$; $0\ x\ \frac{1}{4}$; $\bar{x}\ \bar{x}\ \frac{1}{4}$; $\bar{x}\ 0\ \frac{3}{4}$; $0\ \bar{x}\ \frac{3}{4}$; $x\ x\ \frac{3}{4}$.	x=0.48.
6	O	in	6(*f*)	: $\frac{1}{2}00$; $0\frac{1}{2}0$; $\frac{1}{2}\frac{1}{2}0$; $\frac{1}{2}0\frac{1}{2}$; $0\frac{1}{2}\frac{1}{2}$; $\frac{1}{2}\frac{1}{2}\frac{1}{2}$.	
12	O	in	12(*j*)	: $x\ y\ \frac{1}{4}$; $\bar{y}$, $x-y$, $\frac{1}{4}$; $y-x$, $\bar{x}$, $\frac{1}{4}$;	
				$\bar{x}\ \bar{y}\ \frac{3}{4}$; y, $y-x$, $\frac{3}{4}$; $x-y$, x, $\frac{3}{4}$;	$x \approx 0.42$.
				$y\ x\ \frac{1}{4}$; $\bar{x}$, $y-x$, $\frac{1}{4}$; $x-y$, $\bar{y}$, $\frac{1}{4}$;	$y \approx 0.22$.
				$\bar{y}\ \bar{x}\ \frac{3}{4}$; x, $x-y$, $\frac{3}{4}$; $y-x$, y, $\frac{3}{4}$.	

Observed (single crystal data) and calculated structure factor values corresponding to the reflections registered in the powder photographs are given in Table 2. The calculated F values for reflections absent in the powder photograph are generally very low ($|F| < 50$ except for F(5 1 $\bar{6}$ 0), which is equal to —70). The agreement is similar in character also for the remaining interferences registered in the single crystal photographs. There are considerable divergences between the observed intensities of the powder photograph and the calculated ones, which, however, may be qualitatively accounted for as being due to orientation effects.

DISCUSSION OF THE STRUCTURE

The structure is built up of WO_6 octahedra throughout connected by having corners in common and arranged in layers normal to the hexagonal axis. The unit dimension parallel to this axis comprises two such layers, which mutually

only show minor displacements of the atoms. The cohesion between subsequent layers (W—W distances of 3.78 Å) is less pronounced than that within the layers (W—W distances of 3.70 Å), which is reflected in the flaky form of the crystals.

Within the layers the WO_6 octahedra are connected to form a regular network of three- and six-membered rings. The characteristic ability of WO_6 octahedra to join corners forming various polygons has previously been demonstrated in several tungsten-oxygen compounds. Thus, the tetragonal potassium tungsten bronze [9] and the closely related tetragonal sodium bronze [10] are built up of three-, four-, and five-membered rings of WO_6 octahedra, while the tungsten oxide $W_{18}O_{49}$ [11] contains three-, four-, and six-membered rings. From this point of view the arrangement of tungsten and oxygen atoms present in the sodium and lithium tungsten bronzes of the perovskite and perovskite-like types [12–15] as well as in the tungsten oxides WO_3 [16,17] and $W_{20}O_{58}$ [18] may be considered as corresponding to tetragons of WO_6 octahedra. Further examples of the broad extent of the possible combinations of the WO_6 octahedra in tungsten-oxygen compounds are offered by the dioxide [19], crystallizing in a strongly distorted rutile lattice, by the paratungstate ion, $W_{12}O_{46}^{20-}$, the structure of which has recently been determined by Lindqvist [20], and by the heteropolytungstates, investigated by Keggin and others [21]. It is obvious that there exists a remarkable analogy between the coupling together of the WO_6 octahedra in the tungsten-oxygen compounds and that of the SiO_4 tetrahedra of the silicate chemistry. It may also be mentioned that discrete WO_6 octahedra recently have been shown to occur in the alkaline-earth tungstates $Me_3^{II}WO_6$ [22].

The alkali atoms of the tungsten bronzes generally stabilize a highly symmetrical arrangement of the WO_6 octahedra. Thus, while the room temperature form of tungsten trioxide represents a highly distorted, low-symmetrical modification of a lattice of ReO_3-type, the insertion of a proper amount of sodium or lithium atoms gives rise to the cubic tungsten bronzes of the perovskite type. With low contents of sodium and lithium the somewhat less regular, tetragonal bronzes of the degenerated perovskite type occur *.

* A similar modification of the distorted lattice of the room temperature form of tungsten trioxide towards the ideal ReO_3-type lattice is likely to occur in the forms stable at higher temperatures, recently shown to exist by Wyart and Foëx and others [23–25]. The crystalline preparations of tungsten blue, H_xWO_3, investigated by Glemser and Naumann [26], also show a similar transition towards an arrangement of ideal ReO_3-type with increasing content of hydrogen. — The WO_6 octahedra within the big blocks, which constitute the major structural elements of the $W_{20}O_{58}$ lattice, correspond to a fairly regular ReO_3-type structure [18]. In this case the occurrence of recurrent dislocations of certain tungsten atoms is likely to partly eliminate the obstacles preventing the trioxide from acquiring the ideal structure.

In a similar way the bulky potassium, rubidium or cesium atoms seem to stabilize the symmetrical, hexagonal array of WO_6 octahedra present in the actual bronze type. (*Cf.* the highly irregular arrangement of WO_6 octahedra filling up the regions between the six-membered rings of the $W_{18}O_{49}$-lattice [11].)

The unit cell dimensions of the hexagonal tungsten bronzes are approximately the same irrespective of the alkali metal being potassium, rubidium, or cesium (*cf.* Table 1), which indicates that the tungsten and oxygen atoms form a rather rigid three-dimensional network. The interstices in this lattice ought to be somewhat less than the size required by the cesium atom, since the unit cell of the cesium bronze increases slightly with increasing alkali content. On the other hand, increasing the content of the positively charged potassium or rubidium atoms, which are too small to fill up the holes of the tungsten-oxygen lattice, ought to cause a contracting effect on the surrounding oxygen polyhedra. This must result in a reduction of the unit cell volume, since it can hardly be counterbalanced by an expansion of the rigid WO_6 octahedra caused by the simultaneous decrease of the average valency of the tungsten atoms. This idea seems to be verified by the observed data for the potassium bronzes, which show a slight contraction of the unit volume with increasing alkali content. The compositions of the rubidium bronze preparations are too close to each other to allow a corresponding judgment for this group of compounds.

COLOUR

It was pointed out by Hägg [12] that the colour of the cubic sodium tungsten bronzes depends on the proportion of quinque- and sexa-valent tungsten atoms present in the lattice. Subsequently it has been stated that the same relation between the colour and average valency of the metal atoms is valid for a great number of tungsten bronzes, tungsten oxides, and molybdenum oxides [8]. This is also true of the hexagonal tungsten bronzes, the colours of which are comparable to that of the tetragonal tungsten bronzes of composition Na_xWO_3 ($x \sim 0.3$).

ELECTRICAL CONDUCTIVITY

Measurements of the electrical conductivity of the cubic sodium tungsten bronze were carried out by Hägg [12], who stated that this substance is an electronic semiconductor. Straumanis and co-workers [14, 27–29] studied various single and mixed bronze systems and found that the cubic lithium tungsten bronze of highest alkali content shows considerable ionic conductivity. This was interpreted as due to the lithium atoms being small enough to be able to slip through the openings between the WO_6 octahedra of the lattice [14].

Values of the electrical conductivity observed for preparations of the hexagonal tungsten bronzes are listed in Table 1. The measurements, which were made at room temperature only, had to be carried out with the bronze in powder form. The sample was kept in a glass tube between two electrodes under such a high pressure that a maximum reading of the conductivity value was obtained. The figures are thus rather approximate but represent minimum values of the conductivity. They are of the same magnitude as the values observed for samples of tetragonal potassium tungsten bronze [29] and of cubic sodium tungsten bronze of relatively high alkali content [27]. It seems highly probable that the conductivity of the hexagonal tungsten bronzes, containing the largest alkali atoms, is purely electronic in character.

SUMMARY

The dark blue tungsten bronzes obtained by reducing acid mixtures of tungsten trioxide with potassium, rubidium, or cesium tungstate have been shown to have the general formula Me_xWO_3 (x variable with a theoretical upper limit of 1/3). The crystal structure of the three compounds, which are isomorphous, has been elucidated. The lattice may be described as consisting of layers, built up of WO_6 octahedra, which are joined by corners to form a pattern of three- and six-membered rings. The layers are mutually connected by the WO_6 octahedra having corners in common. The alkali atoms are distributed in the major interstices between the layers. — The colour and the electrical conductivity of these bronzes are in fair agreement with the corresponding properties of previously investigated alkali tungsten bronzes.

The author wishes to thank Miss Birgitta Blomberg for her valuable assistance in the experimental work. The investigation forms part of a research program on oxides and oxide systems financially supported by the *Swedish Natural Science Research Council.*

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Received April 24, 1952.