ACTA CHEMICA SCANDINAVICA 5 (1951) 372–378

Contribution to the Knowledge of the Alkali Tungsten Bronzes

ARNE MAGNÉLI and BIRGITTA BLOMBERG

Institute of Chemistry, University of Uppsala, Uppsala, Sweden

In the ample literature on alkali tungsten bronzes a great number of different compounds have been reported (*cf.* Gmelin [1] and Mellor [2]). In 1935, however, it was shown by Hägg[3,4] that all sodium tungsten bronzes of cubic symmetry, described by previous authors, are not separate compounds but members of a continuous series of solid solutions corresponding to a phase Na_xWO_3 of variable composition with a very extended homogeneity range. At the theoretical upper limit of x equal to 1 all the tungsten atoms are in the quinquevalent state and the bronze crystallizes with a complete perovskite lattice. With decreasing values of x, statistically distributed, vacant positions occur in the original sodium lattice and a corresponding number of tungsten atoms acquire the valency of six.

As it was thought very likely that the knowledge of other tungsten bronzes was in several respects inadequate an investigation of these compounds was started at this Institute a few years ago. The aim of these studies has been especially to settle the existence and composition of the existing phases and to find their crystal structures. Generally no attempts have been made to find the extension of the homogeneity ranges of the various phases. It has also been thought of interest to correlate the structures of the bronzes with those of certain related compounds recently investigated here, *viz.* oxides of tungsten and molybdenum [5]. On the following pages a survey will be given of results concerning the preparation and composition of the various phases obtained.

Methods of preparation

The general method of preparing tungsten bronzes is by reduction of polytungstates *. This reaction may be carried out in various ways. The original

* The word polytungstate is here used for substances of composition $Me_2O \cdot nWO_3$ ($n > 1$), without regard to whether they are definite compounds or not.

method, introduced by Wöhler[6], involves heating of the polytungstate in a stream of hydrogen. Wright[7] reduced fused polytungstate with tin, zinc or other elements, while Scheibler[8] used electrolytic reduction of the molten material. Brunner[9] heated mixtures of polytungstate and tungsten dioxide *in vacuo*.

In the present investigation syntheses have been carried out utilizing reduction with hydrogen and tungsten dioxide and by electrolysis. The polytungstates were prepared by heating alkali carbonate with tungsten trioxide. Tungsten dioxide was obtained by heating tungsten trioxide mixed in the proper proportion with tungsten powder *in vacuo*. Platinum * or carbon electrodes were used for the electrolytic reductions.

With most of the syntheses impure products were obtained. The purification of the bronzes comprised repeated boiling alternately with concentrated alkali carbonate solution, concentrated hydrochloric acid, and *aqua regia*, and in certain cases a final boiling with a mixture of concentrated nitric acid and hydrofluoric acid.

Identification of the products

All the samples were investigated microscopically and by means of X-ray powder photographs. The latter were recorded in focusing cameras using monochromatized Cu-$K\alpha$ radiation. Exact unit cell dimensions were obtained from photographs taken in Phragmén-Hägg focusing cameras with Cr-K or Cu-K radiation and expressed in true Å units[10].

Methods of analysis

In a recent paper[11] comments and certain improvements of the methods for analysing tungsten bronzes have been reported. The analyses of all the investigated bronzes except the lithium compounds were performed according to those principles. For the latter compounds the applied methods failed to give faithful results, and we have thus refrained from any definite conclusions concerning the compositions of these compounds. Quite recently, however, Straumanis and Hsu[12] have reported that they have overcome the difficulties connected with the analysis of lithium tungsten bronzes, but so far their method has not been tested here.

INVESTICATED COMPOUNDS

The generally adopted idea that the composition of the alkali tungsten bronzes may be represented by the formula Me_xWO_3 has been fully confirmed

* The platinum electrodes were heavily attacked during the electrolyses.

by our chemical analyses and crystal structure investigations. For all bronzes, the structures of which have been hitherto determined, the constant ratio of tungsten atoms to oxygen atoms equal to 1 : 3 is accounted for by the arrangement of the atoms of the lattices. They have all been found to contain a stable framework of WO_6 octahedra mutually connected by having corners in common, every oxygen atom thus belonging to two octahedra.

Lithium tungsten bronzes

The blue lithium tungsten bronzes $Li_2W_4O_{12}$[9] and $Li_2W_5O_{15}$[8,9,13–16] have been reported by previous authors. Blue preparations with lower content of lithium have been considered to consist of mixtures of bronzes (*e. g.* $Li_2W_7O_{21}$)[9].

Perovskite phase. A lithium tungsten bronze, briefly reported in previous papers[5,17], has been synthesized by heating mixtures of lithium polytungstate and tungsten dioxide ($\sim Li_2O \cdot 3WO_3 + 0.3WO_2$) at about 850° C *in vacuo* and also by electrolytic reduction of fused lithium polytungstate ($\sim Li_2O \cdot 2WO_3$, current density at the cathode ~ 0.6 A/cm^2). The product obtained by the first method consisted of a blue or bluish violet crystalline powder, while dark blue crystals of irregular shape were formed by the electrolysis. The powder photographs showed the structure to be of perovskite type and thus isomorphous with that of the cubic sodium tungsten bronze (*v. infra*). The length of the cube edge, being about 3.72 Å, was slightly different for various preparations, thus indicating that the substance has the character of a berthollide. The composition was roughly given to be Li_xWO_3 ($x = 0.4$ or 0.3).

These data have been fully confirmed by the investigations independently carried out by Straumanis and Hsu [12]. These authors furthermore state that the limits of the homogeneity range correspond to values of x equal to 0.57 and 0.31. The two compounds $Li_2W_4O_{12}$ and $Li_2W_5O_{15}$, assumed by previous authors, should thus be members of this series of solid solutions.

Tetragonal phase. In the powder photographs of preparations that had not been reduced as far as those mentioned above, lines of another phase appear together with those of the perovskite phase. The lithium content of the new phase is obviously less than that of the latter. The extra lines are consistent with a tetragonal unit cell with the dimensions $a = 5.14$ Å, $c = 3.80$ Å. The structure is isomorphous with that of tetragonal sodium tungsten bronze II (*v. infra*). This tetragonal lithium tungsten bronze may be identical with a tetragonal phase mentioned by Straumanis and Hsu [12].

Sodium tungsten bronzes

Besides preparations of cubic sodium tungsten bronze of different compositions and colours described by various authors there are also reports of a bronze with the composition $Na_2W_5O_{15}$ forming blue, prismatic needles [15,18] and of samples of blue bronzes of still lower sodium content, assumed to be mixtures of $Na_2W_6O_{18}$ and $Na_2W_7O_{21}$ [9].

Perovskite phase. This phase, investigated by Hägg [4], has been briefly described in the introduction to this paper. It has a very broad homogeneity range ($0.32 \lesssim x \lesssim 0.93$) [4] comprising all the cubic sodium tungsten bronzes reported by previous authors. Later on various values of the limits of the sodium content have been given [19–21]. It must be emphasized that the extension of the homogeneity range may show considerable variations connected with the temperature of preparation of the samples.

Tetragonal phase I. This compound was synthesized by electrolytic reduction of fused sodium polytungstate ($Na_2O \cdot 2.5WO_3$) at about 800° C with a current density at the cathode of 0.3A/cm². The composition of the sample, consisting of rather long blue needles, was $Na_{0.38}WO_3$. For a specimen of similar appearance, prepared by Hägg using another polytungstate mixture ($Na_2O \cdot 3WO_3$), analysis gave the formula $Na_{0.28}WO_3$. This phase evidently is identical with the bronze $Na_2W_5O_{15}$ described by previous authors. Powder photographs showed the symmetry of the structure to be tetragonal and gave the unit cell dimensions $a = 12.102$ Å, $c = 3.752$ Å for the former sample and $a = 12.094$ Å, $c = 3.748$ Å for the latter. These dimensions, however, correspond to a substructure of the real lattice, as was obvious by the occurrence in amply exposed single crystal photographs of very weak reflections, indicating the true unit cell to have the axial lengths $a' = a\sqrt{2}$ and $c' = 2c$. The crystal structure was found to be closely related to that of the tetragonal potassium tungsten bronze (*v. infra*). A report of these studies has been previously published [22].

Tetragonal phase II. By electrolyzing sodium polytungstates richer in tungsten trioxide than those mentioned above ($Na_2O \cdot 3.5WO_3$), dark blue, prismatic crystals of a tungsten bronze were obtained, previously not characterized. The colour after grinding was bluish green. The composition of one of the preparations was found to be $Na_{0.10}WO_3$. The structure was tetragonal with the unit cell dimensions $a = 5.25$ Å, $c = 3.90$ Å. A structure determination has been carried out and will be published elsewhere [23]. The structure is closely related to that of the perovskite phase.

Potassium tungsten bronzes

A violet potassium tungsten bronze, forming needle-shaped crystals, has been described by several authors. Opinions have diverged concerning the formula of this compound, the compositions $K_2W_3O_9$ [15] and $K_2W_4O_{12}$ [13,24,25] being reported. Blue preparations of lower potassium content have been considered to consist of mixtures of bronzes ($K_2W_5O_{15}$, $K_2W_6O_{18}$, $K_2W_8O_{24}$) [9], but similar products have also been regarded as containing potassium octotungstate [13].

Tetragonal phase. By reducing potassium polytungstates with hydrogen at about 600° C a bronze was obtained in the form of very small reddish-violet needles. The alkali content of the product was found to be dependent on the composition of the polytungstate used. Thus by reducing $K_2O \cdot 1.2WO_3$ a preparation K_xWO_3 ($x = 0.57$) was obtained while a polytungstate $K_2O \cdot 3.5WO_3$ gave a bronze with x equal to 0.475. This phase thus seems to be identical with the violet bronze reported by previous authors, the formula $K_2W_4O_{12}$ falling within and $K_2W_3O_9$ slightly outside the observed homogeneity range. The dimensions of the tetragonal unit cell were found to be $a = 12.317$ Å, $c = 3.841$ Å for the preparation $K_{0.57}WO_3$ and $a = 12.285$ Å, $c = 3.833$ Å for $K_{0.475}WO_3$. By heating a mixture of polytungstate and tungsten dioxide ($K_2O \cdot 2WO_3 + 0.5WO_2$) *in vacuo* rather large crystals of the tetragonal phase were obtained, contaminated by the dark blue hexagonal phase *(v. infra)*. The crystal structure of the tetragonal bronze has been determined and described in a previous paper [26].

Hexagonal phase. By heating a mixture of potassium polytungstate and tungsten dioxide ($K_2O \cdot 6WO_3 + 3WO_2$) at about 1100° C *in vacuo* the dark blue compound mentioned above was prepared in a pure state in the form of irregularly shaped crystals. The composition of the product was found to be $K_{0.27}WO_3$ in close agreement with the formula $K_2W_8O_{24}$ proposed by Brunner [9]. The analysis definitely excluded the possibility of this substance being an octotungstate(VI) [13], thus confirming the view of Brunner *. The powder photographs were consistent with an hexagonal unit cell with the dimensions $a = 7.40$ Å, $c = 7.56$ Å. The density value of 6.702 given by Brunner would correspond to a cell content of 6(5.9) formula units of $K_{0.27}WO_3$. An attempt to find the crystal structure of this compound will be made in the near future.

---

* The results of the analyses were 4.45 % K + 95.74 % WO_3 = 100.19 % in total, while the contents corresponding to an octotungstate, $K_2O \cdot 8WO_3$, are 4.01 % K and 95.17 % WO_3. For the hexagonal rubidium and cesium tungsten bronzes analyses gave the following results (values corresponding to the octotungstate formulae within brackets): 9.10 % Rb + 91.00 % WO_3 = 100.10 % (8.37 % Rb and 90.85 % WO_3) and 15.44 % Cs + 84.66 % WO_3 = 100.10 % (12.44 % Cs and 86.81 % WO_3).

Rubidium and cesium tungsten bronzes

According to Schäfer [25] a mixture of blue-violet rubidium tungsten bronze ($Rb_2W_4O_{12}$) and dark blue rubidium octotungstate can be prepared by heating rubidium polytungstate in a stream of hydrogen. Nothing is said in the literature about cesium tungsten bronzes.

Hexagonal phases. By heating a mixture of rubidium polytungstate and tungsten dioxide ($Rb_2O \cdot 2WO_3 + 0.3WO_2$) at about 1050° C *in vacuo* dark blue crystals of a rubidium tungsten bronze were obtained. The composition of the preparation was found to be $Rb_{0.27}WO_3$. The same product could also be prepared by reducing $Rb_2O \cdot 3WO_3$ with hydrogen at about 600° C. Powder photographs showed this bronze to be isomorphous with the hexagonal potassium tungsten bronze, the unit cell dimensions of the former being $a = 7.39$ Å, $c = 7.54$ Å. It seems probable that this phase is identical with the „octotungstate" described by Schäfer. No substance corresponding to the compound $Rb_2W_4O_{12}$ has been observed in our experiments.

Similarly by heating cesium polytungstate and tungsten dioxide ($Cs_2O \cdot 4WO_3 + 0.5WO_2$) at about 950° C *in vacuo* a dark blue cesium tungsten bronze of composition $Cs_{0.32}WO_3$ was prepared. This phase was found to be isomorphous with the hexagonal potassium and rubidium bronzes. The unit cell has the dimensions $a = 7.42$ Å, $c = 7.63$ Å.

SUMMARY

A number of alkali tungsten bronzes has been synthesized in pure form. The preparations have been investigated analytically and by means of X-ray methods and the results have confirmed the view that these compounds have the general formula Me_xWO_3 ($x<1$). The observed phases have been found to comprise the majority of alkali tungsten bronzes reported by previous authors. The following structural types have been found:

perovskite type, represented by lithium and sodium [4] bronzes,

degenerated perovskite type of tetragonal symmetry, appearing in the lithium and sodium bronze systems at low alkali metal contents,

tetragonal potassium tungsten bronze type (a related sodium compound of considerably lower alkali content shows a superstructure in comparison with this type), and

hexagonal potassium tungsten bronze type with representatives also appearing in the rubidium and cesium bronze systems.

The authors wish to thank Professor G. Hägg for his kind interest in the investigation. The work has been supported by a grant from the Swedish Natural Science Research Council, which is gratefully acknowledged.

REFERENCES

1. Gmelins *Handbuch der anorganischen Chemie.* 8th ed. Wolfram. System-Nummer 54. (1933) Berlin.
2. Mellor, J. W. *A comprehensive treatise on inorganic and theoretical chemistry.* XI (1931) London.
3. Hägg, G. *Nature* 135 (1935) 874.
4. Hägg, G. *Z. physik. Chem.* B 29 (1935) 192.
5. Magnéli, A. *Nova Acta Regiae Soc. Sci. Upsaliensis* [4] 14 (1950) no. 8.
6. Wöhler, F. *Pogg. Ann.* 2 (1824) 345.
7. Wright, H. *Ann.* 79 (1851) 221.
8. Scheibler, C. *J. prakt. Chem.* 83 (1861) 273.
9. Brunner, O. *Dissert.* Zürich (1903).
10. Bragg, W. L. *J. Sci. Instruments* 24 (1947) 27.
11. Magnéli, A. *Arkiv Kemi* 1 (1949) 273.
12. Straumanis, M. E., and Hsu, S. S. *J. Am. Chem. Soc.* 72 (1950) 4027.
13. von Knorre, G. *J. prakt. Chem.* [2] 27 (1883) 49.
14. Feit, W. *Ber.* 21 (1888) 133.
15. Hallopeau, L.-A. *Ann. Chim. Phys.* [7] 19 (1900) 92.
16. Stavenhagen, A. *Ber.* 32 (1899) 3064.
17. Magnéli, A., and Nilsson, R. *Acta Chem. Scand.* 4 (1950) 398.
18. Philipp, J. *Ber.* 15 (1882) 499.
19. van Duyn, D. *Rec. trav. chim.* 61 (1942) 669.
20. Straumanis, M. E. *J. Am. Chem. Soc.* 71 (1949) 679.
21. Rabes, I., and Schenk, R. *Z. anorg. Chem.* 259 (1949) 201.
22. Magnéli, A. *Arkiv Kemi* 1 (1949) 269.
23. Magnéli, A. Unpublished.
24. von Knorre, G., and Schäfer, E. *Ber.* 35 (1902) 3407.
25. Schäfer, E. *Z. anorg. Chem.* 38 (1903) 142.
26. Magnéli, A. *Arkiv Kemi* 1 (1949) 213.

Received December 20, 1950.