A Lithium Tungsten Bronze of Perovskite Type

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In a recent paper from this institute [1] the existence of a cubic lithium tungsten bronze of perovskite type was briefly mentioned. As the work on this subject must be postponed for some time, a few more of the details obtained so far will be given here.

The compound has been synthesized in two different ways: *a)* according to the method introduced by Brunner [2] by heating mixtures of lithium tungstate, tungsten trioxide, and tungsten dioxide *in vacuo* at about 850° C, and *b)* by cathodic reduction of fused acid lithium tungstate as was first done by Stavenhagen [3]. Attempts to prepare the compound by reducing acid lithium tungstate with hydrogen were not successful as inhomogeneous products were obtained. The products were purified by repeated alternate boiling with concentrated potassium carbonate solution, concentrated hydrochloric acid, and aqua regia and finally with a mixture of concentrated nitric acid and a small amount of hydrofluoric acid. In this way a dark blue or bluish violet crystalline powder was obtained by the first method, while the electrolytic reduction gave dark blue crystals of irregular shape. The samples were tested for purity by means of X-ray powder photographs and microscopic examination.

The powder photographs were taken in focusing cameras using Cu-K radiation. All observed reflections are consistent with a cubic unit cell of perovskite type. This lithium bronze is evidently isomorphous with the cubic sodium tungsten bronze, Na_xWO_3, described by Hägg [4]. The length of the cube edge, being about 3.72 Å, is slightly different for various preparations, probably due to the lithium content of the compound not being constant. The formula may thus be written Li_xWO_3. Values and limits of x cannot be given for the present for lack of analytical data. However, if the relation between colour and average valency of the molybdenum or tungsten atoms shown to exist for a great number of oxides and bronzes [1] is also valid for this lithium bronze, the blue colour might indicate an x value of 0.3 or 0.4 for the investigated preparations.

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2. Brunner, O. *Dissert.* Zürich (1903).
3. Stavenhagen, A. *Ber.* **32** (1899) 3064.
4. Hägg, G. *Z. physik. Chem.* **B 29** (1935) 192.

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control experiments it was established that the generated methyl alcohol had no effect on the indicator blank. As an example, in Fig. 1, a curve for two parallel experiments is reproduced. The two series of points fall on the same straight line. If $k = \frac{2.303}{t} \log c_0/c_x$, the slope of the line gives a value of k of $8.04 \cdot 10^{-3}$. Another experiment ($c_0 = 0.01$ M) with 0.05 M hydrochloric acid at 25.0° C gives $k = 4.25 \cdot 10^{-3}$.

1. Samén, E. *Arkiv Kemi* **1** (1949) no. 26.
2. Backer, H. J. *Rec. trav. chim.* **49** (1930) 1107.

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